VOL. XX. MAY, 1898. NO. 5.

AMERICAN

CHEMICAL JOURNAL

A DETERMINATION OF THE ATOMIC WEIGHT OF PRASEODYMIUM, AND OF NEODYMIUM.

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The determinations of the atomic weight of the supposed element didymium, have been discussed to a greater or less extent by Meyer and Seubert,[1] Ostwald,[2] and Clarke.[3] Yet, for the sake of completeness and reference, a brief account of what has been done will be given here.

Marignac[4] precipitated the sulphuric acid from a solution of didymium sulphate by means of barium chloride, but found that when the precipitate was boiled in the presence of even a large excess of the chloride, it still contained didymium sulphate. His best results were obtained by precipitating the didymium from a solution of the sulphate, as oxalate, by means of oxalic acid, and decomposing the oxalate at a very high temperature, to avoid the presence of superoxide. He found, as the mean of five determinations, 143.58 ($SO_3 = 80$) as the atomic weight of didymium.

Hermann[5] precipitated the didymium from a solution of the sulphate, as oxalate, by means of ammonium oxalate, decom-

[1] Atomgewichte, 218. [2] Lehrb. allgem. Chem., 1, 70.
[3] A Recalculation of the Atomic Weights, 351–353.
[4] Ann. chim. phys. [3], 27, 231; 38, 151. [5] J. prakt. Chem., 82, 387.

posed the oxalate by heat, and weighed the oxide. He found 146.7 for the atomic weight of the element. The determination of the chlorine in the chloride gave 142.2 as the atomic weight of didymium. Zschiesche[1] decomposed the sulphate to the oxide, and obtained the value 141.8. Erk,[2] using the method of Hermann, found the atomic weight of didymium to be 142.35. He also precipitated the sulphuric acid from the solution, out of which the didymium had been separated by oxalic acid, as barium sulphate. By this method the atomic weight was found to be 142.29. He employed, in addition, the method which Marignac first used, precipitating the sulphuric acid directly from a hydrochloric acid solution of didymium sulphate, as barium sulphate, and obtained the figure 143.46. This is necessarily erroneous, since, as Marignac has pointed out, some didymium sulphate is always carried down under these conditions.

Hillebrand[3] converted a weighed amount of the metal into the nitrate, and then into the oxide, and found 144.78 (O=16), as the atomic weight of didymium. By the aid of the Bunsen ice calorimeter he found that the specific heat of pure metallic didymium was 0.04563. This number multiplied by 144.78 gives 6.60, which agrees with the law of Dulong and Petit. This shows that the atomic weight of didymium must be expressed by a number very nearly of the order of that given above, and not by two-thirds of this amount. Therefore, didymium forms the normal sesquioxide Di_2O_3, and not DiO.

Cleve[4] heated the oxide in a stream of hydrogen to remove all superoxide, and from the sesquioxide thus obtained he synthesized the sulphate. As a mean of six determinations, he obtained the value 147.01, maximum 147.23, minimum 146.65.

The presence of samarium was later discovered in the above material. This was removed,[5] and ten new syntheses of the sulphate effected from the pure sesquioxide. The mean of these new results is 142.33, maximum 142.49, minimum 142.03.

[1] J. prakt. Chem., **107**, 75.
[2] Ztschr. anal. Chem., **10**, 509.
[3] Ann. der. Phys. Pogg., **158**, 71.
[4] Bull. Soc. Chim., **21**, 246.
[5] *Ibid*, **39**, 289.

Brauner[1] effected the synthesis of the sulphate from the oxide, and as the mean of three determinations obtained the value 146.58.

Later,[2] he made five determinations with samples prepared in different ways, and found as a mean 145.42, with a difference between the highest and lowest value of 0.22. While these results agree fairly well with one another, they differ about a unit from his earlier result, which makes it probable that the oxide first employed contained some element of higher atomic weight. He tested this point as follows:

Some of the didymium oxide used in the first series of experiments, which gave 146.58 as the atomic weight of the element, was fractionally precipitated with ammonia. The atomic weight of didymium, as determined with the fraction which was precipitated last, was found to be 145.40, which made it more probable that the substance first used contained an element with higher atomic weight. Further fractionation confirmed this point beyond question. Brauner concluded that the atomic weight of didymium was probably 145.2 to 145.4.

Bauer[3] synthesized the sulphate from the oxide, and obtained, as a mean of four determinations, the value 142.74.

Auer Von Welsbach[4] showed that didymium is not an element, but is composed of at least two, thereby invalidating all the preceding results, without, however, affecting the value of the methods which had been used. He effected the separation by fractional crystallization of the double nitrate of ammonium and didymium, from strong nitric acid, and repeating the process several thousand times. The one element forms green salts and green solutions, and the other rose-colored solutions, and the salts are the color of amethyst. To the former he gave the name *praseodymium*, and to the latter *neodymium*. Both the emission and absorption spectra of the two elements are different, but their sum is the same as the corresponding spectrum of didymium.

The elements resemble one another more closely than in

[1] Ber. d. chem. Ges., **15**, 109; Monatsh. Chem., **3**, 14.
[2] Monatsh. Chem., **3**, 499; J. Chem. Soc., **43**, 278.
[3] Inaugural Dissertation, Freiburg, 1884. [4] Monatsh. Chem., **6**, 477.

any other known cases. Their conduct towards oxygen is, however, very different. Neodymium forms only the sesquioxide Nd_2O_3, while praseodymium forms most readily, the oxide Pr_4O_7; indeed, this is formed whenever the oxalate, or sesquioxide, is heated in contact with air. It is easily reduced to the sesquioxide in a stream of hydrogen gas. Von Welsbach, without giving any details or even the method employed, assigned the atomic weight 143.6 to praseodymium, and 140.8 to neodymium.

Later, Crookes[1] stated that, "although I have not split up didymium into the two earths, or groups of earths, which are described by Dr. Auer, other processes of fractionation gave me, so to speak, other cleavage planes, or lines of scission through the compound molecule, didymium. * * * * Neodymium and praseodymium must not be considered as actual chemical elements, but only the names given to two groups of molecules, into which the complex molecule didymium splits up, by one particular kind of fractionation."

The material used in carrying out the piece of work about to be described, was furnished me, with unusual generosity, by Mr. Waldron Shapleigh, of the Welsbach Light Company, Gloucester, New Jersey, who has also made many valuable suggestions in connection with the separation of the elements. I wish to state here, that this work was made possible only by the abundance of the comparatively pure praseodymium and neodymium compounds, which Mr. Shapleigh placed at my disposal.

The Atomic Weight of Praseodymium.

About 1¼ kilograms of the double nitrate of praseodymium and ammonium were furnished me by Mr. Shapleigh. It was analyzed spectroscopically by means of the large Rowland spectroscope, with a concave grating of about 21 feet focal length, by Dr. W. J. Humphreys, and found to contain small amounts of neodymium, cerium, and lanthanum. No trace of any of the other rare elements, whose presence might reasonably be expected, could be detected.

The double nitrate, which had been thus far purified, was

[1] Nature, **34**, 266.

treated as follows: The entire mass was dissolved in water containing a little nitric acid, and evaporated until crystals appeared. The solution was then cooled until a part of the double nitrate separated. This was filtered from the solution, and since it contained more of the lanthanum, was discarded. The solution was then strongly acidified with nitric acid, and evaporated on the water-bath until, on cooling, about two-thirds of the total material crystallized out. This was the purest praseodymium, and was used for further crystallization. The mother-liquor was filtered from these crystals and discarded, because it was richest in neodymium. The original substance was thus separated by fractional crystallization into three parts, the first and last being discarded, and the second preserved as the purest material. The second portion was then treated exactly as the original substance, being separated into three portions by fractional crystallization, and the middle portion again treated in the same manner. This process was repeated twenty-one times. Any impurities, such as calcium, iron, etc., were separated from the middle fraction of the last crystallization, by precipitating the praseodymium with oxalic acid, in the presence of nitric acid. Only praseodymium oxalate is thrown down under these conditions. The oxalic acid used, was purified by repeated crystallization from a mixture of alcohol and ether, to remove acid salts, and contained no detectable trace of either potassium or sodium. The water used in dissolving the praseodymium salt, also in washing the oxalate, and in all the processes of crystallization, had been especially purified by distilling, first from acid permanganate, and then from alkaline, in the apparatus described by myself and Mackay.[1] In all of this work the solutions were never allowed to come in contact with glass vessels while warm, but only with porcelain.

The precipitation of the oxalate was effected by pouring very slowly the hot, dilute solution of the double nitrate of praseodymium and ammonium, into a hot, dilute solution of oxalic acid, with vigorous stirring. The oxalate thus pre-

[1] This JOURNAL, **19**, 91; Ztschr. phys. Chem., **22**, 237.

cipitated, separated in a form which could be easily washed free from impurities. A portion of this oxalate was subjected to spectrum analysis, and was found to contain a trace of neodymium, cerium, and lanthanum. The amount of the neodymium present, was determined by comparing the intensity of the absorption bands of the neodymium in a solution of the praseodymium salt of known concentration, with the absorption bands of the neodymium salt, also of known concentration. A very concentrated solution of the double nitrate of praseodymium and ammonium was prepared, and the intensity of the absorption bands of neodymium noted. Then the solution of the double nitrate of neodymium and ammonium was diluted until the absorption bands were of the same intensity of those of the neodymium in the praseodymium salt. The amount of the neodymium in the solution of the neodymium salt was known, since this was prepared of standard concentration. The amount of the neodymium in the praseodymium salt could thus be calculated directly. By comparing the intensity of the absorption bands of neodymium in the two solutions, by bringing first the one and then the other into the field of the Steinheil spectroscope, we could estimate very closely the amount of the neodymium present in the praseodymium salt. It was found to be 0.06 per cent. and could, therefore, be disregarded.

A further attempt was made to remove the trace of cerium and lanthanum, since the exact amounts present could not be determined accurately, because of the absence of sufficiently intense absorption bands. The oxalate of praseodymium, purified as just described, was decomposed by heat into the oxide, in a platinum vessel. The oxide was dissolved in nitric acid, the excess of acid evaporated, and the solution of the nitrate poured into a large volume of pure boiling water. The cerium present would then be precipitated as the basic nitrate, and a slight cloudiness in the solution was observed. This was repeated until the solution, in a large volume of water, was perfectly clear.

The solution of praseodymium nitrate was evaporated, and enough purified ammonium nitrate added, to form the double salt. The double nitrate was then crystallized from a very

strong nitric acid solution, far stronger than had been hitherto used, in order to remove the remaining trace of lanthanum. This was repeated several times.

The solution of the double nitrate of praseodymium and ammonium, thus purified, was poured into oxalic acid, after being acidulated with nitric acid, as before described, to remove any calcium, iron, etc., which might have gotten in, during the separation of the traces of cerium and lanthanum. The oxalate was washed with the greatest care, converted into the oxide, and this again analyzed spectroscopically by Mr. L. E. Jewell. No trace of cerium was detected, and only a trace of lanthanum.

This oxide, which was used in the following determinations, was blackish-brown, and had the general properties of a superoxide. When dissolved in sulphuric acid there was a copious evolution of oxygen. It was easily reduced to the sesquioxide when heated in a stream of hydrogen gas. When the superoxide was reduced to the sesquioxide it lost 2.5 per cent. of oxygen, corresponding closely to the composition Pr_4O_{11}, which is the composition of the superoxide described by Von Welsbach.[1] It is thus quite clear that the superoxide of praseodymium which I employed, agreed in all of its essential properties with that isolated and used by Von Welsbach.

The method first employed consisted in dissolving the superoxide in sulphuric acid, evaporating the solution of the sulphate to dryness, and heating it in a platinum vessel, to a temperature above the boiling-point of sulphuric acid. The sulphate was then weighed, dissolved in water to form a very dilute solution, strongly acidified with hydrochloric acid, and the sulphuric acid precipitated by means of barium chloride. It was hoped that by using a very dilute solution, strongly acidified, it would be possible to precipitate all of the sulphuric acid as the barium salt. Several determinations were made, but the results obtained were so discordant as to be entirely valueless. The presence of praseodymium was shown in the precipitate, even after it had been boiled with excess of barium chloride for a considerable time. This fact

[1] Monatsh. Chem., 6, 489.

had been pointed out by Marignac,[1] but it was hoped that by working in very dilute solutions, which had been strongly acidified, the difficulty could be overcome. It could not, and the method had to be abandoned as entirely useless for the purpose of an atomic weight determination.

The method adopted consisted in reducing the superoxide to the sesquioxide in an atmosphere of hydrogen, and converting the sesquioxide into the sulphate. The details of the process are as follows :

A weighed amount of the superoxide was placed in a porcelain boat, and this within a hard-glass tube, which rested upon a combustion furnace. A stream of hydrogen gas, which had been washed in a solution of sodium plumbate, to remove hydrogen sulphide, and in silver nitrate, to remove arsine, was dried over calcium chloride, and passed through the tube. The superoxide was easily reduced to the sesquioxide on heating. The sesquioxide was allowed to become perfectly cold in the current of hydrogen, and boat and contents were then removed from the tube and weighed. The boat containing the sesquioxide was then returned to the glass tube and reheated in an atmosphere of hydrogen. In no case was there any change in weight caused by the second heating.

A platinum crucible was placed within a ground-glass stoppered weighing-tube, which was then closed and weighed. The sesquioxide was poured from the boat into the crucible, and the whole was reweighed. This gave the weight of the sesquioxide used in a determination.

A considerable excess of sulphuric acid, of medium concentration, was added to the crucible. An equal volume of the sulphuric acid used, was placed in a weighed platinum crucible, evaporated to dryness, and heated exactly as in carrying out a determination, to see whether there was any appreciable residue left behind. In no case did the weight of the crucible increase more than 0.00005 gram, which was therefore negligible. The platinum crucible, containing the oxide and sulphuric acid, was placed in an air-bath constructed of thick sheet copper, and closed at the bottom by a piece of

[1] *Loc. cit.*

very thick sheet copper. The sides of the bath were thickly covered with asbestos paper. The platinum crucible rested upon a porcelain triangle, about an inch from the bottom of the air-bath. Heat was applied to the bath, very gently at first, to avoid all spattering, and then increased, until the solution of the sulphate had evaporated nearly to dryness. Then the bath was heated more strongly, and finally raised to a temperature above the boiling-point of sulphuric acid. The sulphate was maintained at this temperature for some hours, and then weighed. It was reheated and reweighed, and this continued until constant weight was reached. To determine whether only the normal sulphate was present, purified ammonium carbonate was added, and the crucible and contents again heated above the boiling-point of sulphuric acid. There was no change in the weight of the sulphate, showing that only the normal sulphate of praseodymium was present. The sulphate thus prepared was perfectly soluble in water. I was completely unable to verify the observation of Bailey,[1] who stated that "the sulphate was made into a paste with sulphuric acid and heated at 360°. * * * An approach to a constant weight was manifest, but variations amounting to a milligram or more occurred, and with each successive increase of temperature the loss was accelerated. No range of temperature could be found within which the salt remained perfectly constant."

I found that the weight of the sulphate remained perfectly constant through a considerable range of temperature, provided the temperature to which it had been heated was sufficient to remove all the excess of sulphuric acid, and decompose any acid sulphate. It is possible that Bailey did not heat the sulphate, or in his case the mixture of praseodymium and neodymium sulphates, to a temperature sufficiently high to leave only the normal sulphate. This is the only way I can account for the result which he obtained.

The crucible containing the sulphate was removed from the air-bath as quickly as possible and placed in the weighing-tube. This was closed and placed in a desiccator over phosphorus pentoxide and allowed to cool. The sulphate was then

[1] J. Chem. Soc., **51**, 676.

weighed in the closed tube, which is necessary, since it absorbs moisture rapidly from the air.

The Results.

	Pr_2O_3.	$Pr_2(SO_4)_3$.	$3(SO_3)$.	$\left\{\begin{matrix}O=16\\S=32.07\end{matrix}\right\}$ At. wt. Pr.	$\left\{\begin{matrix}O=15.88\\S=31.83\end{matrix}\right\}$ At. wt. Pr.
1	0.5250	0.9085	0.3835	140.42	139.37
2	0.6436	1.1135	0.4699	140.50	139.45
3	0.7967	1.3788	0.5821	140.38	139.33
4	0.7522	1.3018	0.5496	140.38	139.33
5	0.7788	1.3473	0.5685	140.53	139.48
6	0.6458	1.1172	0.4714	140.54	139.49
7	0.6972	1.2062	0.5090	140.51	139.46
8	0.7204	1.2464	0.5260	140.49	139.44
9	0.8665	1.4990	0.6325	140.54	139.49
10	0.6717	1.1624	0.4907	140.40	139.35
11	0.7439	1.2873	0.5434	140.42	139.37
12	0.6487	1.1224	0.4737	140.47	139.42
	8.4905	14.6908	6.2003	140.46	139.41

The average of the individual determinations is 140.46 when oxygen = 16, or 139.41 when oxygen = 15.88. The difference between the highest and lowest value is 0.16. This series represents all of the determinations which were made, with the exception of two, which were lost by accident and never completed.

The atomic weight of praseodymium, as calculated from the total oxide used, and total sulphate formed, is 140.47 when O = 16, or 139.41 when O = 15.88.

The sesquioxide, prepared by reducing the superoxide in a current of hydrogen, always liberates a small amount of gas when dissolved in sulphuric acid. This is probably occluded hydrogen. The amount of gas thus set free was determined approximately, and found to be so small that it could be disregarded.

The atomic weight of praseodymium, as here determined, may be taken as 140.45 when oxygen = 16, or 139.4 when oxygen = 15.88. This result lays no claim to very great accuracy, because of the apparent impossibility of obtaining an absolutely pure praseodymium compound. However, considering the result of the careful spectroscopic analysis which

was made of the material which I employed, and all the errors which could possibly have entered into the determinations, I see no reason to think that the result can differ from the true atomic weight of praseodymium by more than 0.2 of a unit.

The Atomic Weight of Neodymium.

Somewhat more than 2 kilograms of the double nitrate of neodymium and ammonium were furnished me by Mr. Shapleigh. This was analyzed spectroscopically, and found to contain praseodymium and also a trace of lanthanum. The substance was further purified by fractional crystallization, as described for praseodymium. The entire material was dissolved in water, to which a little nitric acid had been added, and evaporated, until, on cooling, about $\frac{1}{15}$ to $\frac{1}{20}$ crystallized out. A considerable volume of nitric acid was then added, and the larger part of the double salt allowed to separate on further concentrating the solution. The mother-liquor was then carefully filtered from the crystals. The first and third fractions were discarded, and the second preserved for further treatment. The middle fraction was then treated exactly as the original substance had been, was separated into three fractions, and the middle one preserved and again treated in the same manner. This process was repeated twenty-seven times.

The middle fraction of the last crystallization was dissolved in water, strongly acidified with nitric acid, and poured into a dilute solution of oxalic acid, in the same manner as described under praseodymium. This would separate such common impurities as iron, calcium, etc. The oxalate was washed with great thoroughness, dried, and decomposed in a platinum crucible over the blast-lamp. The oxide of neodymium, thus prepared, was again analyzed spectroscopically. It was found to contain praseodymium and a trace of lanthanum. The same method was employed to separate the trace of lanthanum, as in the case of the praseodymium salt.

The praseodymium which remained in the double salt of neodymium, could not be separated by any known method, and must therefore be determined. The amount present was

ascertained with considerable accuracy by studying the intensity of the absorption bands, and comparing these with the absorption bands of the pure praseodymium salt, of known concentration. The exact method is that described under praseodymium. It was found that the double nitrate of neodymium and ammonium contained 1.6 per cent. of the double nitrate of praseodymium and ammonium.

After the lanthanum was separated the neodymium was again precipitated as the oxalate, with oxalic acid, in the presence of nitric acid, by the method already described. The oxalate was converted into the oxide by heating in a platinum crucible over the blast-lamp. The oxide thus obtained was analyzed spectroscopically, special attention being given to the presence of thorium. The only impurity which could be detected was praseodymium, the amount of which had already been determined.

The oxide of neodymium, obtained from the oxalate, does not possess any property of a superoxide as such. It dissolves in sulphuric acid without the evolution of oxygen. When heated in a current of hydrogen exactly as the oxide of praseodymium obtained from the oxalate, it does not change in weight. When hot, the oxide has a marked bluish color, which, however, disappears on cooling. It will thus be seen that the substance which I employed in determining the atomic weight of neodymium, had all the properties described by Von Welsbach,[1] as characteristic of the sesquioxide of neodymium.

The method employed in determining the atomic weight of neodymium was the same, in general, as that used in the case of praseodymium. After it had been found that the oxide obtained from the oxalate did not change in weight when heated in a current of hydrogen, this part of the process was abandoned. The oxide was, however, heated in the platinum crucible just before weighing, and allowed to cool in a desiccator over phosphorus pentoxide, to remove every trace of moisture. The method of synthesizing the sulphate from the oxide, and heating and weighing the sulphate, was the same as employed with praseodymium.

[1] Monatsh. Chem., 6, 489.

The Results.

	Nd_2O_3.	$Nd_2(SO_4)_3$.	$3SO_3$.	$\{O = 16, S = 32.07\}$ At. wt. Nd.	$\{O = 15.88, S = 31.83\}$ At. wt. Nd.
1	0.8910	1.5296	0.6386	143.58	142.50
2	0.7880	1.3530	0.5650	143.51	142.43
3	0.9034	1.5509	0.6475	143.57	142.49
4	0.7668	1.3166	0.5498	143.51	142.43
5	0.8908	1.5296	0.6388	143.49	142.41
6	0.8848	1.5194	0.6346	143.46	142.38
7	0.8681	1.4903	0.6222	143.57	142.49
8	0.8216	1.4103	0.5887	143.62	142.54
9	0.8531	1.4646	0.6115	143.56	142.48
10	0.8711	1.4957	0.6246	143.50	142.43
11	0.8932	1.5332	0.6400	143.62	142.54
12	0.8893	1.5268	0.6375	143.55	142.47
	10.3212	17.7200	7.3988	143.55	142.47

The average of the 12 determinations is 143.55 when oxygen = 16, or 142.47 when oxygen = 15.88. The difference between the highest and lowest value is 0.16. Three determinations were lost by accident. The atomic weight of neodymium, calculated from the total amount of oxide used, and sulphate formed, is 143.55 when oxygen = 16, or 142.47 when oxygen = 15.88.

The value of the atomic weight of neodymium thus found must be corrected for the presence of praseodymium, which has an atomic weight about 3 units lower. The final value, which, from my work, I should assign to the atomic weight of neodymium, is 143.6 when oxygen = 16, or 142.52 when oxygen = 15.88. I think this value can be regarded as accurate to within about the same limits as indicated in the case of praseodymium.

The oxide of neodymium, prepared as above described, liberated a small amount of gas, presumably air, when dissolved in sulphuric acid. But since this work lays no claim to the last degree of accuracy, due chiefly to the impossibility of effecting complete separations of the rare elements, such corrections were found to be less than the necessary experimental error.

The values which I obtained for the atomic weights of

praseodymium and of neodymium differ widely from those given by Von Welsbach.[1] It is impossible to determine from the paper of Von Welsbach, what he regarded as the atomic weight of oxygen, but since no statement is made, the presumption is in favor of 16. The following comparison will show how widely the two results differ:

	Von Welsbach.	My Results.
Pr	143.6	140.45
Nd	140.8	143.6

There is a discrepancy of about three units in the case of each element. Indeed, if my values were reversed for the two elements, they would not differ widely from those of von Welsbach.

It is not possible to account satisfactorily for the difference between my results and those of Von Welsbach, since the latter has given no details pertaining to his determinations. The fact that if either set of results were interchanged for the two elements, they would agree with the other, suggests that possibly the discrepancy arose in a typographical error in the paper of Von Welsbach, in which his values are recorded as tentative, and in less than a line.

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February, 1898.

Contribution from the Chemical Laboratory of the University of Minnesota.

VERATRINE AND SOME OF ITS DERIVATIVES.

BY GEORGE B. FRANKFORTER.

The substance commonly known in pharmacy as veratrine, varies widely in its composition, chemical, physical, and physiological properties. Until recently, it has been exceedingly difficult to obtain different samples with the same general properties. The introduction of the so-called "Merck veratrine" has changed matters somewhat, although samples of the Merck alkaloid have been found to vary considerably in their general properties.

One of the chief causes of this exceptional variation, is the extreme difficulty with which the alkaloid crystallizes, thus

[1] Monatsh. Chem., 6, 490.

almost excluding one of the most important means of purification. Another, and perhaps the most important reason for this wide variation, lies in the fact that almost everyone of the early investigators of the "veratria" has given the name to a different alkaloid or to a mixture of alkaloids.

Pelletier and Caventou[1] first obtained from *Veratrum sabadilla*, an amorphous base which was afterward shown to be a mixture of several alkaloids. For some time, this substance was sold as a medicine under the name "veratria."

Later, Couerbe,[2] in an examination of the sabadilla, obtained three distinct substances. One of these, the most abundant, was amorphous but formed crystallizable salts. He called the base veratrine. Two analyses gave numbers for the formula, $C_{34}H_{49}N_3O_6$.

Merck,[3] in an examination of the same substance, found that when dissolved in very dilute alcohol and allowed to evaporate spontaneously, it crystallized in fine, white, efflorescent needles. His analyses gave numbers for the formula, $C_{64}H_{99}N_3O_{16}$. Several salts were made and analyzed, corresponding well with the above formula.

Schmidt and Köppen[4] obtained from the crude alkaloid, by a method similar to that given by Merck, a crystallizable base which they called veratrine, seven analyses of which gave numbers for the formula, $C_{32}H_{49}NO_9$. These three substances were known and used as veratrine.

Wright and Luff[5], in a series of experiments on the alkaloids of the *veratra*, have thrown much light on what was hitherto apparently a mass of contradictions. A sharp distinction was made between the several bases which at that time were known as veratrine. They showed that the substance described by Merck was not identical with the veratrine of Couerbe, but that with the exception of a single nitrogen determination, it corresponded well with the base which Schmidt and Köppen had in hand. By a special method of extraction, however, they obtained a substance which corresponded well with Couerbe's veratrine. They

[1] Ann. chim. phys. [II], **14**, 69.
[2] *Ibid* [II], **52**, 352.
[3] Ann. Chem. (Liebig), **95**, 200.
[4] *Ibid*, **185**, 224.
[5] J. Chem. Soc. (London), **33**, 338.

gave to it the formula, $C_{37}H_{53}NO_{11}$. On saponifying the substance with alcoholic sodium hydroxide, veratric acid and a base which closely resembled cevine were obtained:

$$C_{37}H_{53}NO_{11} + H_2O = C_9H_{10}O_4 + C_{28}H_{45}NO_8.$$

In their examination of crystallized veratrine, Wright and Luff showed that it was entirely different from the above-mentioned veratrine, and that it probably did not exist in an isomeric form. By treating with alcoholic potassium hydroxide, cevadic acid and a new base, cevine, were obtained according to the following reaction:

$$C_{32}H_{49}NO_9 + H_2O = C_8H_8O_2 + C_{27}H_{43}NO_8.$$

From this reaction crystallized veratrine was called cevadine.

Bossetti,[1] in a discussion of veratrine, found it to exist in the above-mentioned isomeric forms—a crystalline and a non-crystalline. By treating the crystalline form with alcoholic barium hydroxide, angelic acid, and a base of the formula, $C_{27}H_{43}NO_8$, were formed. He called the base cevidine:

$$C_{32}H_{49}NO_9 + H_2O = C_8H_8O_2 + C_{27}H_{43}NO_8.$$

The amorphous form, by the same treatment, yielded veratric acid and veratroine

$$2C_{32}H_{49}NO_9 + 2H_2O = C_9H_{10}O_4 + C_{55}H_{92}N_2O_{16}.$$

Ahrens,[2] in an examination of crystallized veratrine or cevadine, obtained both cevadic and angelic acids by treating the alkaloid with alkalies. With alcoholic potassium hydroxide, cevadic acid was formed, and with barium hydroxide, angelic acid. Cevadic acid was likewise formed with concentrated hydrochloric acid.

Of special interest is the result of a dry distillation of the alkaloid. At 200° C., a colorless acid was obtained which was identified as tiglic acid. At the same time a base was obtained which was identified as β-picoline. As this experiment is of great importance toward determining the constitution of the alkaloid, it has been repeated. The results obtained are, however, somewhat different.

While a careful comparison of cevadine with the crystal-

[1] Arch. Pharm. (1883), 82. [2] Ber. d. chem. Ges., **23**, 2700.

lized veratrine has shown them to be identical, and while historically, perhaps, cevadine should take precedence, nevertheless, from the fact that cevadine is the common veratrum alkaloid used at present, it seems advisable to retain the name which associates the alkaloid with the genus of plants from which it is obtained. The name veratrine has, therefore, been retained in the following account of the work.

Experimental Part.

The veratrine with which the following experiments have been made is of a light gray color, and appears, when highly magnified, as imperfect granular crystals. It is slightly soluble in water, very soluble in methyl, ethyl and amyl alcohols, in ether, acetone, chloroform and carbon disulphide. It appears, upon the evaporation of any of these solutions, as a light-brown varnish. On stirring this varnish-like mass with water, it changes to a granular, semicrystalline mass. It refused to crystallize from alcohol. The powdered form has a peculiar bitter, rasping taste, producing a certain numbness of the tongue if taken in very small quantities. This peculiarity readily distinguishes it from any of the other alkaloids. It is a violent sternutatory, producing intense irritation of the nasal mucous membrane. It retards the action of the heart, even when taken in small quantities. It gives a slightly alkaline reaction, which is intensified when the alkaloid is dissolved in alcohol. It gives with dilute nitric acid a pale yellow solution; with concentrated nitric acid, a brown color, and a strong odor of acetic acid. With concentrated sulphuric acid, it produces an orange-red color, which, on standing for some time, becomes fluorescent; with a great excess of acid, it becomes intensely red in transmitted light. With concentrated hydrochloric acid, it immediately produces a blood-red color, which seems to be permanent. It changes, however, to a dark brown color on heating. If the red solution from the hydrochloric acid is rendered slightly alkaline with ammonia, the color changes to a dirty green, even when the alkaloid is present in very small quantities. The melting-point after purification was 146°–148° C.

In order to determine whether or not the substance in hand

was identical with that described by Merck and Ahrens, analyses of the free base, as well as of the gold double salt were made.

No reference was made by the above-named investigators to the water of crystallization. Three determinations were made, the mean of which agreed for one molecule of water.

I. 0.2401 gram of alkaloid, dried at 100°–102°, lost 0.0081 gram H_2O.

II. 0.3108 gram of alkaloid, dried at 100°–102°, lost 0.0103 gram H_2O.

III. 0.5124 gram of alkaloid, dried at 100°–102°, lost 0.0164 gram H_2O.

	Calculated for $C_{32}H_{49}NO_9.H_2O$.	Found. I.	II.	III.
H_2O	3.00	3.33	3.31	3.2

Combustions of the dried substance gave the following:

I. 0.1933 gram gave 0.4572 CO_2, and 0.1441 gram H_2O.

II. 0.2060 gram gave 0.4874 CO_2, and 0.1513 gram H_2O.

	Calculated for $C_{32}H_{49}NO_9$.	Found. I.	II.
C	64.96	64.8	64.53
H	8.29	8.4	8.16

The purity of the alkaloid was further shown by the properties and the melting-point of the gold double salt which melts, according to Merck and Ahrens, at 178°–180°. The recrystallized double salt was found to have the melting-point 178°–182° (uncorr.). The melting-point of the base itself is not given by the above-mentioned investigators. A gold determination gave the following results:

0.2462 gram dried salt gave 0.05171 gram Au.

	Calculated for $C_{32}H_{49}NO_9HCl.AuCl_3$.	Found.
Au	21.08	21.00

Determination of Methoxyl.

Wright and Luff,[1] in their work on the alkaloids of the sabadilla, stated that cevadine (which is undoubtedly identical with the Merck veratrine) contains one hydroxyl group.

[1] J. Chem. Soc. (London), **33**, 338.

They verified the assumption by the introduction of a benzoyl group, forming a monobenzoyl veratrine,

$$C_{32}H_{45}(C_7H_5O)NO_9.$$

The presence of tiglic acid or methylcrotonic acid was also indicated by its formation when the base was heated with water at 200°. They therefore ascribed to the base the following formula:

$$C_{27}H_{41}NO_8\begin{cases}OH\\ OOC-C(CH_3)=CH-CH_3\end{cases}.$$

It would appear from this formula that the alkaloid contains no methoxyl group, although no record of such a determination has been given. In order to determine definitely the presence or absence of the methoxyl group, two analyses were made by the Zeisel method with the following results:

I. 0.2461 gram of dried substance gave 0.0698 gram AgI.

II. 0.2021 gram of dried substance gave 0.0636 gram AgI.

	Calculated for $C_{31}H_{46}NO_8(OCH_3)$.	Found. I.	II.
OCH_3	4.19	4.16	4.72

The Iodides of Veratrine.

As stated by Ahrens,[1] veratrine absorbs bromine readily, forming a tetrabromide, $C_{32}H_{49}NO_9Br_4$. It was prepared by triturating veratrine with strong bromine water, when a yellow powder was formed which was purified by filtering and washing with warm water. It proved to be insoluble in water but readily soluble in alcohol, ether, chloroform, and acetone.

On treating the tetrabromide with dilute potassium hydroxide, two bromine atoms were readily removed, a light yellow dibromide, $C_{32}H_{49}NO_9Br_2$, being formed.

Reference is also made by Bauer,[2] to an iodide of veratrine which was prepared by the action of iodine on a salt of veratrine. The formula given is $C_{32}H_{54}N_2O_8HI_2$.

Veratrine Tetraiodide, $C_{32}H_{49}NO_9I_4.3H_2O$.—A careful examination showed that iodine also combines readily with veratrine forming a series of compounds which in many respects

[1] Ber. d. chem. Ges., **23**, 2700. [2] Arch. Pharm. [III], **5**, 289.

resemble the bromides. By triturating veratrine with a strong alcoholic solution of iodine, a reddish-brown substance was formed which upon examination appeared to be a mixture of several substances. This was also indicated by the varying melting-point. A great excess of iodine was then added and the substance allowed to stand for several days when a beautiful, light-red, crystalline substance was formed melting at 129°–130°. It is very soluble in methyl and ethyl alcohols forming, upon evaporation, a dark-brown, waxy mass. It is soluble in acetone, forming a wax, which upon standing becomes a dark-red powder. It is insoluble in water, benzol, and ether. By treating with sulphurous acid, the red color disappeared and a light yellow powder was formed which was afterward identified as the monoiodide. With dilute ammonia, the same substance is formed, but with concentrated ammonia, a white, gelatinous substance is formed with some of the properties of the free base. An examination showed it to be different from the free alkaloid, although all of the iodine had been removed.

Great difficulty was experienced in the determination of water of crystallization. It was found, after several determinations, that four hours' drying at 100°–102° was necessary to remove the 3 molecules of water present. It was also found that by drying at 104°–106° some of the iodine was driven off. This explained the difficulty in obtaining satisfactory results in the early analyses. A careful determination of moisture was made, the temperature being gradually raised to 114°, with the following results:

2.362	gram	substance	dried	at	100°	for	2	hours	lost 0.082
"	"	"	"	"	100°–102°	"	"	"	" 0.118
"	"	"	"	"	100°–102°	"	"	"	" 0.119
"	"	"	"	"	100°–104°	"	"	"	" 0.152
"	"	"	"	"	100°–104°	"	"	"	" 0.179
"	"	"	"	"	100°–105°	"	"	"	" 0.190
"	"	"	"	"	100°–105°	"	"	"	" 0.224
"	"	"	"	"	100°–105°	"	"	"	" 0.224
"	"	"	"	"	102°–106°	"	"	"	" 0.240
"	"	"	"	"	102°–106°	"	"	"	" 0.247
"	"	"	"	"	104°–107°	"	"	"	" 0.276
"	"	"	"	"	104°–107°	"	"	"	" 0.299
"	"	"	"	"	105°–108°	"	"	"	" 0.327

2.362 gram substance dried at 105°–109° for 2 hours lost 0.341
" " " " " 105°–110° " " " " 0.382
" " " " " 105°–110° " " " " 0.382
" " " " " 110°–112° " " " " 0.389
" " " " " 112°–112° " " " " 0.402
" " " " " 112°–114° " " " " 0.414

The weight appeared to be constant at 110°, even when heated at that temperature for four hours. The substance showed decided indications of decomposition however, at 112°–114°, and at 120° began to frit, changing to an almost black, waxy mass. As will be seen from the above numbers, the substance dried to constant weight at 100° loses 3 molecules of water.

2.362 grams dried at 100° lost 0.118 gram H_2O.

	Calculated for $C_{32}H_{49}NO_9I_4.3H_2O$.	Found.
$3H_2O$	4.68	4.99

It was found, on examination, that the loss which occurred by heating above 102° was due to liberation of iodine, and that by drying at 110° to constant weight, one-fourth of the iodine could be driven off.

2.362 grams substance dried to constant weight at 110° lost 0.382 $I + H_2O$.

	Calculated for $C_{32}H_{49}NO_9I_3 + I + 3H_2O$.	Found.
$I + 3H_2O$	15.7	16.17

An attempt to remove another atom of iodine was unsuccessful, as is indicated by the above experiment, although the loss which occurred between 110°–114° was due to the liberation of iodine.

An analysis of the substance dried at 100° to constant weight was made with the following results:

0.2231 gram of dried iodide gave 0.2834 gram CO_2, and 0.0912 gram H_2O.

	Calculated for $C_{32}H_{49}NO_9I_4$.	Found.
C	34.94	34.64
H	4.45	4.9

Veratrine Triiodide, $C_{32}H_{49}NO_9I_3$.—The red iodide, dried at 110° to constant weight, became a dark-brown, amorphous

powder, which showed no signs of crystallization when treated with water. It is insoluble in ether and much less soluble in methyl and ethyl alcohols than the tetraiodide. It melts at 136°–138°.

Analyses gave the following results:

I. 0.2034 gram substance gave 0.2938 gram CO_2, and 0.1152 gram H_2O.

II. 0.1945 gram substance gave 0.1405 gram AgI.

	Calculated for $C_{32}H_{49}NO_9I_2$.	Found. I.	Found. II.
C	39.5	39.37	....
H	6.36	6.28	....
I	39.2	....	38.6

While it was evident that more than one-fourth of the iodine could be driven off by drying, repeated attempts to obtain the diiodide were unsuccessful.

Veratrine Monoiodide, $C_{32}H_{49}NO_9I$.—By treating the tetraiodide with dilute ammonia, and allowing to stand for several hours in a warm place, the bright-red color disappeared and a light-yellow granular substance was formed. It proved to be insoluble in water, ether, and chloroform, but very soluble in methyl and ethyl alcohols. A bright-yellow powder is formed on evaporating off the alcohol. It does not form the waxy mass which characterizes the tetraiodide. It was obtained from a dilute alcoholic solution as a fine crystalline powder with a melting-point of 212°–214°. It contains 2 molecules of water, which were removed by drying at 100°.

0.3782 gram substance dried at 100° lost 0.018 gram H_2O.

	Calculated for $C_{32}H_{49}NO_9I + 2H_2O$.	Found.
$2H_2O$	4.77	4.76

An analysis gave the following:

0.1763 gram dried substance gave 0.0583 gram AgI.

	Calculated for $C_{32}H_{49}NO_9I$.	Found.
I	17.68	17.87

On digesting with strong ammonia for a short time the iodide was completely removed, and a white insoluble gelatinous substance was formed, which at first was regarded as

the free alkaloid. An examination showed that it differed from veratrine in general appearance and solubility. It melted at 189°.

Other Compounds.

Chloralhydroveratrine, $CCl_3CH\begin{cases}O(C_{32}H_{48}NO_8)\\O(C_{32}H_{48}NO_8)\end{cases}$.—As stated by Wright and Luff,[1] veratrine, heated at 100° with twice its weight of benzoic anhydride, is converted into a monobenzoylveratrine, $C_{32}H_{48}(C_7H_5O)NO_9$. The formation of this compound proved the presence of one hydroxyl group. The writer repeated the experiment in order to determine whether or not more than one hydroxyl group existed in the alkaloid. The impossibility of making more than the mono derivative was sufficient evidence that but one group existed. It was found, however, that this group was so loosely held that it could be replaced by treating with almost any anhydride. Chloral was found to react vigorously on the alkaloid, producing a sort of effervescence. In an excess of chloral the alkaloid dissolves. With a smaller quantity, a waxy mass is formed, which readily changes to a creamy-white, granular powder. This powder was washed thoroughly with ether to remove the free chloral. The substance in the pure state was almost white and crystalline. A determination showed the reaction to be quantitative. Five grams of the veratrine gave 6.1 grams of the pure chloral compound. It is insoluble in ether and chloroform, but very soluble in water and alcohol. It melts at 220°. In its physiological properties, it resembles veratrine. It is a most powerful sternutatory, producing violent irritation of the nasal mucous membrane. In minute quantities it affects the eyes, causing intense pain and contracting the pupils. It is a remarkable local irritant. Applied to the moistened skin, and rubbed, it produces blisters. It is readily decomposed by alkalies. Ammonia decomposes it forming chloral hydrate and veratrine. It is hygroscopic, taking up 2 molecules of water if exposed to the air for some time. The water can readily be removed by drying at 100°.

Analyses gave the following numbers:

[1] J. Chem. Soc., **32**, 351.

I. 0.2394 gram dried substance gave 0.5280 gram CO_2, and 0.1530 gram H_2O.

II. 0.1692 gram dried substance gave 0.0502 gram AgCl.

	Calculated for $CCl_3CH(OC_{32}H_{48}NO_8)_2$.	Found. I.	II.
C	60.38	60.2	....
H	7.38	7.1	....
Cl	8.2	....	7.35

The alkaloid formed by the action of ammonia upon the substance was carefully examined in the hope of finding the isomeric base of Schmidt and Köppen. Although the base seemed to have a few different properties from the original veratrine, the gold double salt had exactly the properties and melting-point of the original gold salt.

Veratrine Methyl Iodide, $C_{32}H_{49}NO_9.CH_3I$.—From the resemblance of veratrine to the alkaloids narcotine and narceine, it was believed that it would form a compound with methyl iodide. It was found, on treating the base with excess of methyl iodide, that the substance readily dissolved with the exception of a very small quantity of gelatinous matter, which proved to be an impurity. By allowing the filtered solution to stand for some hours, or by heating on a water-bath with a reflux condenser, the whole of the base precipitated out as a solid, yellow, crystalline mass. The reaction was completed at the end of an hour on the water-bath, but it required several days at the ordinary temperature to convert it completely into the iodide. Excess of the methyl iodide was then evaporated off, and the veratrine compound treated with ether to remove any trace of the unchanged alkaloid. The iodide thus obtained was a light-yellow, crystalline powder, insoluble in ether and chloroform, and soluble in methyl and ethyl alcohols. It is soluble in hot water, from which it can be obtained as an almost white, crystalline powder. It melts at 210°–212° with apparent decomposition.

It contains 1½ molecules of water of crystallization which can be removed by drying at 100°.

I. 0.3547 gram dried to constant weight at 100° lost 0.0132 gram H_2O.

II. 1.1180 grams dried to constant weight at 100° lost 0.0431 gram H_2O.

	Calculated for $C_{32}H_{49}NO_9.CH_3I + 1\frac{1}{2}H_2O$.	Found. I.	II.
$1\frac{1}{2}H_2O$	3.55	3.72	3.85

Analyses gave the following numbers:

I. 0.2131 gram dried substance gave 0.4243 gram CO_2, and 0.1440 gram H_2O.

II. 0.2034 gram dried substance gave 0.0638 gram AgI.

	Calculated for $C_{32}H_{49}NO_9CH_3I$.	Found. I.	II.
C	54.03	54.28	....
H	7.1	7.35	....
I	17.32	....	16.94

Veratrine Methyl Hydroxide, $C_{32}H_{49}NO_9.CH_3OH$.—It was found that the iodine in the veratrine methyl iodide could be removed by treating with sodium or potassium hydroxide. The iodide was dissolved in water and dilute sodium hydroxide cautiously added. The solution soon began to turn brown and after several hours complete decomposition had taken place. Examination showed that two distinct substances had been formed—a waxy substance which refused to crystallize, and a crystalline substance which was sparingly soluble in water. The reaction seemed deep-seated, but it is probably closely associated with that given by Wright in the preparation of cevine by saponification.

A solution of the methyl iodide compound was again treated with freshly precipitated silver oxide and warmed. It was found that above 45° the solution again turned brown, indicating decomposition. The experiment was repeated without warming the solution. Five grams of the methyl iodide compound were placed in a shaking-flask with 200 cc. water, an excess of silver oxide added, and shaken for twelve hours at the ordinary temperature. At the end of that time the reaction seemed to be complete. The silver iodide and excess of silver oxide were removed by filtration. An attempt to concentrate a part of the clear solution by evaporating on a water-bath proved unsuccessful, for between 40° and 65° decomposition began, and in a half hour the whole solution became almost black.

A second portion of the clear solution was evaporated at the ordinary temperature. At the end of three days a residue was obtained as a white granular powder. The substance proved to be exceedingly unstable, turning gray and finally brown on gently warming. It is soluble in water, methyl and ethyl alcohols, and in acetone; slightly soluble in ether and chloroform. It differs materially from veratrine. It is not sternutatory, and appears to be physiologically inactive. It changes to a brown mass between 80° and 90°, but does not finally melt until the temperature is raised to 188°–190°. It contains water of crystallization, which was removed by heating in an air-bath at 60° for two hours. More satisfactory results, however, were obtained by drying over sulphuric acid *in vacuo*.

0.3958 gram dried to constant weight, lost 0.0320 gram H_2O.

	Calculated for $C_{32}H_{45}NO_9.CH_3+3H_2O$.	Found.
$3H_2O$	8.2	8.09

0.2022 gram dried substance gave 0.4828 gram CO_2, and 0.1557 gram H_2O.

	Calculated for $C_{33}H_{48}NO_9.CH_3$.	Found.
C	65.45	65.13
H	8.43	8.01

The apparent change which took place in the substance on drying is evidently deep-seated. The white granular substance on drying became a fine, light-gray, amorphous powder which is only slightly soluble in water. These changes, together with the comparative ease with which the substance decomposes, indicate that a part of the water exists as water of constitution. This supposition is confirmed by the analyses.

Veratrine Methyl Hydroxy Hydrochloride, $C_{32}H_{49}NO_9.CH_3OH.HCl$.—Veratrine methyl hydroxide is very soluble in dilute acids and readily decomposed by strong acids. Sulphuric acid decomposes it, changing it first to a bright-red color, and finally, with decomposition, to a black, tar-like mass. Hydrochloric acid gives a red color if the acid is strong. Very

dilute acid dissolves it, leaving a perfectly clear solution. If this clear solution is allowed to evaporate spontaneously, a light-gray granular powder is formed. It is soluble in water, and can be obtained by spontaneous evaporation. It is soluble in methyl and ethyl alcohols. It forms a light, amber-colored varnish on evaporating off the alcohol. It is very unstable, decomposing below 100°. It seemed to change upon standing over sulphuric acid for some time.

0.2065 gram substance, dried over sulphuric acid, gave 0.4444 gram CO_2, and 0.1311 gram H_2O.

	Calculated for $C_{32}H_{49}NO_9.CH_3OH.HCl$.	Found.
C	60.00	58.67
H	8.24	6.6

It is evident that the water of constitution is held more firmly here than in the free base.

Gold Double Salt, $(C_{32}H_{49}NO_9.CH_3OH.HCl)AuCl_3$.—An attempt to make the gold double salt from the hydrochloride did not prove successful. A decomposition took place on adding the gold chloride, apparently caused by excess of acid. A better method was found by treating the methyl hydroxide compound with gold chloride which had been rendered slightly acid with hydrochloric acid. A beautiful, lemon-yellow, crystalline powder was formed. It was filtered off, washed with hot water, and dried on an unglazed porcelain plate. The substance thus purified melted at 149°. It is soluble in alcohol, but sparingly soluble in water, ether, and chloroform. It is comparatively stable, remaining unchanged at 110°. A determination of water of crystallization was not made. A gold determination gave the following:

0.1716 gram dried salt gave 0.0362 gram Au.

	Calculated for $(C_{32}H_{49}NO_9.CH_3OH.HCl)AuCl_3$.	Found.
Au	20.37	21.09

Veratrine Ethyl Bromide, $C_{32}H_{49}NO_9.C_2H_5Br$.—Veratrine dissolves readily in ethyl bromide, and combines slowly to form the bromide. It was found that heating on a water-bath with reflux condenser for six hours was necessary to convert it all into the ethyl compound. At the end of the

reaction, the excess of ethyl bromide was evaporated off, leaving the veratrine ethyl bromide as a light-yellow, amorphous mass. By treating with water and stirring for some time, the substance was obtained in crystalline form. It is sparingly soluble in water, but readily soluble in methyl and ethyl alcohols. It decomposes readily. It shows signs of decomposition at 60°, and at 100° it seems completely changed. It does not finally melt, however, until a temperature of 160° is reached. The substance purified by boiling water was dried and analyzed. The result showed that decomposition had taken place, and that a tetrabromide of veratrine was formed. The odor of ethylene was noticed during the boiling. Analysis of the substance thus treated with water gave the following numbers:

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I. 0.2270 gram dried substance gave 0.4591 gram CO_2, and 0.1603 gram H_2O.

II. 0.2228 gram dried substance gave 0.0200 gram AgBr.

	Calculated for $C_{32}H_{49}NO_9C_2H_5Br$.	Found. I.	Found. II.
C	42.15	42.55	....
H	5.38	7.84	....
Br	35.06	....	38.73

Veratrine Allyliodide, $C_{32}H_{49}NO_9.C_3H_5I$. — By digesting veratrine with allyl iodide on a water-bath for several hours, a solid, but slightly waxy-looking, substance was formed. The excess of iodide was removed and the substance washed thoroughly with ether. The iodide thus formed appeared partially crystallized, but changed, on standing in the air, to a semiwaxy mass. Exposed for some time to the air, or when stirred with water, the substance again becomes granular. The substance was finally obtained pure by dissolving in a small quantity of alcohol and precipitating with excess of ether. It thus appears as an almost white, crystalline powder. It is soluble in methyl and ethyl alcohols, and acetone. It melts at 235°–236° C., and contains 1 molecule of water which can be driven off at 100° C.

I. 0.1990 gram dried substance gave 0.4000 gram CO_2, and 0.1202 gram H_2O.

II. 0.3022 gram dried substance gave 0.0954 gram AgI.

	Calculated for $C_{23}H_{41}NO_9.C_3H_5I$.	Found. I.	II.
C	55.29	54.81	....
H	7.1	6.71	....
I	16.73	....	17.04

An attempt to obtain the free base by shaking with silver oxide was unsuccessful. The solution turned brown at the ordinary temperature and had the odor of allyl alcohol.

Several experiments have been made by heating the alkaloid at different temperatures. In each case a beautifully crystallized substance was obtained which gave all the characteristics of veratric acid. Experiments are now being carried on along this line.

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Contributions from the Sheffield Laboratory of Yale University.

LIX.—ON THE ACTION OF HYDROGEN SULPHIDE UPON VANADATES.

By James Locke.

The fact that pentavalent vanadium, in contradistinction from niobium and tantalum, the other members of the group to which this element belongs in the Periodic System, readily forms salts derived from sulphovanadic acids, was first shown conclusively by Krüss and Ohnmais[1] in 1891. These authors investigated very thoroughly such sulphovanadates as they were able to prepare by the wet methods and isolated a number of well-crystallized compounds, such as $(NH_4)_3VS_4$, $Na_3VS_3O + 5H_2O$, $Na_3VO_2S + 10H_2O$, etc. These experiments were supplemented, in 1893, by some work carried out by Krüss[2] alone, on the formation of the same class of salts in reactions in the dry way.

By fusing vanadium pentoxide with sodium carbonate and a large excess of sulphur, until the latter was nearly driven off, and then washing the residue alternately with carbon disulphide and alcohol, he obtained as a residue a brownish-red, crystalline powder. This dissolved readily in water, forming a deep-red or purple solution, and showed the various other properties of the salt, Na_3VOS_3, which in the hydrated form he had previously obtained in the wet way.

[1] Ann. Chem. (Liebig), **263**, 40–72. [2] Ztschr. anorg. Chem., **3**, 264.

Halberstadt[1] has shown that vanadium trichloride can readily be obtained by the direct action of chlorine upon the trisulphide. This reaction suggested to me the possibility of preparing the same substance directly from a sodium or potassium vanadate, by first converting the latter into a sulpho-salt free from oxygen, and then treating the latter with chlorine.

With this end in view, I first submitted sodium orthovanadate, Na_3VO_4, to the action of hydrogen sulphide. The reaction did not proceed exactly as I had hoped, but as the behavior of vanadates upon ignition in an atmosphere of hydrogen sulphide has not hitherto been investigated, a communication of my results may be of some interest. A weighed quantity of the orthovanadate, very carefully dried, was introduced, in a porcelain boat, into a combustion tube, and first submitted to the action of the gas in the cold. A reaction at once set in, but owing to the protective coating of sulphovanadate formed upon the salt, it soon ceased. In order to obtain a homogeneous product, it was found necessary to heat the boat at a temperature of from 500°–700°. At this temperature the absorption of the hydrogen sulphide was almost violent, and care was required to prevent loss due to the spattering of the molten salt. The reaction subsided in a short time, although repeated weighings showed that a slight absorption was still taking place, and the contents of the boat continued slowly to gain in weight for some hours.

The final result was as follows:

	Grams.
Weight of sulphovanadate formed	1.4256
" " Na_3VO_4 taken	1.1390
Increase in weight	0.2866
	= 26.04 per cent.

The increase calculated for the reaction,

$$Na_3VO_4 + 3H_2S = Na_3VOS_3 + 3H_2O,$$

is 26.07 per cent. The product possessed all the characteristic properties which Krüss had previously observed in the salt Na_3VOS_3, and was undoubtedly identical with that compound.

[1] Ber. d. chem. Ges., 15, 1619 (1882).

The fact that both by his method and the above, a complete substitution of sulphur for oxygen could not be obtained in the ortho salt, led me to make a similar experiment with sodium pyrovanadate, $Na_4V_2O_7$. An analogous reaction would here lead to the formation of a salt containing two residual atoms of oxygen. This was found to be the case. The hydrogen sulphide was allowed to pass over the molten salt for six hours; the latter was then weighed, and subsequently treated with the gas for two hours more. No gain was observed to have taken place after the first weighing:

	Grams.
Weight of product	1.1974
" " $Na_4V_2O_7$ taken	0.9536
Increase	0.2438
	= 25.67 per cent.
Calculated increase, $Na_4V_2O_7$ to $Na_4V_2O_5S_5$	= 25.93 " "

This compound, which was not described by Krüss, resembles very closely the other sulphovanadates of the alkali metals. It is easily fusible to a dark, brownish-red liquid, which on cooling solidifies to a highly crystalline mass, the latter being very similar to potassium permanganate in color and luster. When the heated salt is exposed to the air it at once takes fire, giving off sulphur dioxide and yielding as a residue sodium hypovanadate. The salt is exceedingly hygroscopic, and when first dissolved in water forms a deep reddish-purple solution. This changes rapidly in color, however, hydrogen sulphide being given off, and the solution, after passing through various shades of red and pink, becomes colorless. The formation of a colorless sodium vanadate solution in this way would indicate that the first decomposition reaction is simply one of gradual substitution of oxygen for sulphur in the sulphovanadate, according to the equation,

$$Na_4V_2O_5S_5 + H_2O = Na_4V_2O_5S_4 + H_2S, \text{ etc.}$$

Reduction of the vanadic acid to the vanadyl state takes place only subsequently; the solution then turns to green, and finally blue, with deposition of free sulphur.

The gradual passage of the sulphovanadate into the vana-

date is accompanied by a remarkable alteration in the color of the free sulphovanadic acid which separates out on addition of hydrochloric acid. When obtained from a freshly prepared solution, this precipitate is black; from one which has been standing a short time it comes down dark-yellow; and from the nearly oxidized solution it is of a pale orange color. This transition in color from the acids containing much sulphur to those containing little is well seen in the products obtained when a combustion tube is filled with sodium vanadate and submitted to the action of hydrogen sulphide for an hour or two. At first the entire contents of the tube became uniformly brown. But, as heat is applied and the water formed in the anterior portion of the tube reacts with the sulpho-salt in the posterior end, the latter gradually loses color again. The acids obtained by treating the solution of successive portions of the product then show the same gradations in color as do those obtained as before described. Unfortunately, all these acids are so unstable as to render their isolation in the pure state practically impossible. Several attempts were made to obtain them, but without success. Sulphur determinations in a number of precipitates, after careful washing with carbon disulphide, gave values lying between those calculated for the compounds $H_4V_2O_5S_5$ and $H_4V_2O_4S$, but they pointed to the presence of no single acid.

Finally, it must be remarked that in company with Mr. J. S. North, I have tried to prepare the sulphovanadates of several of the heavy metals by the above method. The substitution seems in this case to be less complete than when sodium or potassium vanadate is used, this being probably due to the fact that the vanadates of the heavy metals are not fusible. Lead vanadate alone yielded what seemed to be a definite compound. On subjecting lead pyrovanadate to the action of hydrogen sulphide at a full red heat, the salt at first fused and then solidified again to a crystalline, black powder of high luster. It was then found to have gained 5.31 per cent. in weight. The increase calculated for the conversion of $Pb_2V_2O_7$ into $Pb_2V_2O_5S_2$ is 5.01 per cent., and it is probable, therefore, that the latter is the formula of the product.

NEW HAVEN, February, 1898.

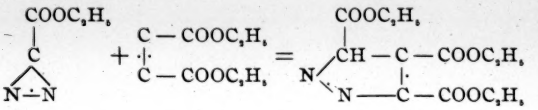
ON THE FORMATION OF IMIDO-1,2-DIAZOL DERIVATIVES FROM AROMATIC AZIMIDES AND ESTERS OF ACETYLENECARBOXYLIC ACIDS.

By A. Michael, F. Luehn, and H. H. Higbee.

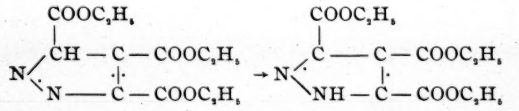
Several years previous to the discovery of hydrazine one of us[1] endeavored to obtain this base by introducing a nitro group into phenylhydrazine, and treating the nitro product with alkalies or acids. At the same time, a series of experiments were made to reduce phenylazimide, but it was found impossible to effect a reduction of this substance without its breaking down to aniline; a decomposition which had been previously described. The reduction of phenylazimide was again attempted, some years later, in a different manner; starting with the idea that if the nitrogen-chain could be broken by addition of some reagent, it might be possible to reduce, and then decompose, the addition-product. Phenylazimide showed itself to be indifferent, at a moderate temperature, to reagents that, in other compounds, are added to unsaturated nitrogen, and at a higher temperature it decomposed. On the other hand, the tendency of nitrogen and carbon to form five-membered rings, showed itself in the remarkable ease with which phenylazimide can be added to esters of $\Delta\alpha\beta$-acids of the acetylene series, and this reaction forms the subject of the present paper. These addition-products no longer show the instability that characterizes the tri-nitrogen-ring, but they are stable towards heat and towards most reagents. It is possible to reduce them, but the hydrogen is added to the unsaturated carbons, and the attempt to effect a further reduction, by the use of strong reducing agents at a higher temperature, was followed by the breaking down of the ring to aniline. The reaction between phenylazimide and acetylenedicarboxylic ester presents a striking analogy to that of diazoacetic and acetylenedicarboxylic esters.[2] The latter reaction takes place by disruption of linkage between carbon and nitrogen to form a five-membered ring, the other possible re-

[1] A. Michael: Ber. d. chem. Ges., 19, 1386.
[2] Buchner: Ann. Chem. (Liebig), 273, 214.

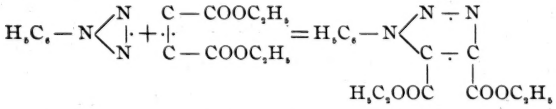
action being less favored, as it would lead to the formation of a four-membered ring :



Owing to the accumulation of negative groups around the methine of this primary product, its hydrogen is very reactive, and, as the product also contains an easily reducible azo-group, a spontaneous atomic rearrangement occurs, in which the methine-hydrogen passes over to the most negative of the nitrogen atoms, with consequent shifting of unsaturation :



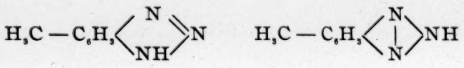
It is evident from the constitution of our addition-product that an intramolecular conversion of the azo into a hydrazine derivative is not possible, as the product does not contain hydrogen in the ring :



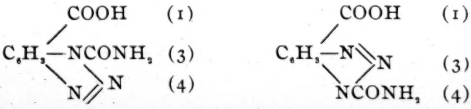
In the above reaction there is a possibility of a four-membered ring being formed, and, although from theoretical reasons, such a ring formation seems improbable, it is desirable to connect the substances we have obtained with imidodiazol derivatives obtained by a different method. Several months previous to the preliminary notice[1] on this reaction, Bladin[2] published a short note on the oxidation of azimidotoluene, in which he described a triazoldicarboxylic acid obtained in this manner. The constitution of this acid depends on that of azimidotoluene, and there are two formulas that have been assigned to it :

[1] A. Michael : J. prakt. Chem. [2] **48**, 94. [2] Ber. d. chem. Ges., **26**, 545.

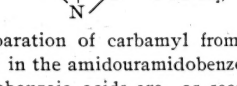
I. II.



The first of these was given by Kekulé,[1] but it was subsequently rejected by Griess,[2] as he found that the same carbamylazimidobenzoic acid[3] is formed from the isomeric 1,3,4- and 1,4,3-amidouramidobenzoic acids, whereas, according to Kekulé's interpretation of the reaction, different carbamylazimido acids should be formed:

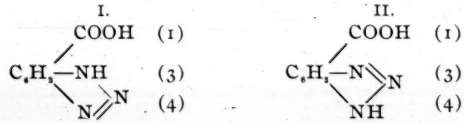


Unfortunately Griess published only a preliminary note on this work, so that a strict proof of the identity of the products obtained from the isomeric acids is wanting. It is also difficult to understand the formation of a compound having the constitution which Griess assigned to carbamylazimidobenzoic acid,



as it implies a separation of carbamyl from the nitrogen to which it is joined in the amidouramidobenzoic acids. If the carbamylazoimidobenzoic acids are, as seems not unlikely, isomeric, but very similar products, it would not be difficult to understand that the azimidobenzoic acids

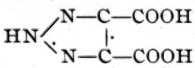
I. II.

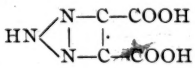


[1] Lehrb. org. Chemie, II, 739. [2] Ber. d. chem. Ges., **15**, 1879.

[3] Griess called this compound azimidouramidobenzoic acid, which is evidently a misnomer, as it does not contain an uramido group. If the radical of carbamic acid is called, according to the usual manner of designating an acid radical, carbamyl, the above name correctly represents the constitution of the substance.

should pass over into one stable modification, it being by no means impossible that a substance with the constitution I. would pass over into that of II. by intramolecular reduction, and consequent shifting of linkage or *vice versa*. Accordingly, whether Kekulé's or Griess' conceptions of the constitution of azimidotoluene is accepted, the constitution of Bladin's acid may be represented as follows :





To ascertain whether the compound from phenylazimide and acetylenedicarboxylic ester is a derivative of the same ring as Bladin's acid, we oxidized the aromatic nucleus to two carboxyls, after having introduced a nitro group into it and conversion of this into an amido group, and we found the dibasic acid thus formed to be identical with Bladin's triazoldicarboxylic acid.

In the reaction of phenylazimide towards acetylenedicarboxylic ester we have the analogy with diazoacetic ester, where the link between carbon and nitrogen is severed, as this addition-product undoubtedly does not contain a tri-membered ring, which would be the case if the addition went by union of unsaturated nitrogens to unsaturated carbons. However, when one considers the tendency of nitrogen to form a tri-ring, it is by no means impossible that a five-membered triazol ring, containing two nitrogens joined together to form a tri-ring, may exist.[1] In this paper we shall consider our products as derived from an open five-membered ring, but we cannot consider this view of their constitution as having been definitely established, and we believe it is more a question of probability than of exact proof.

Action of Phenylazimide[2] *on Methyl Acetylenedicarboxylate.*

If these substances are allowed to stand for some days at ordinary temperature, large crystals are slowly deposited, but under these conditions the addition takes place very slowly. The reaction occurs somewhat more quickly if the mixture is placed in strong sunlight, but this acceleration may be due

[1] A somewhat analogous constitution is supposed to exist in the ketines.

[2] Phenylazimide should be made from phenylhydrazine, freshly distilled in a

to a rise in temperature, and not to the actinic influence of sunlight. The addition proceeds quite rapidly at 100°, and to prepare the substance equivalent amounts of phenylazimide and acetylenedicarboxylic methyl ester, diluted with an equal weight of carbon tetrachloride, are heated to 100° in a flask connected with an inverted cooler for five hours. On cooling a copious precipitate is deposited, which, filtered and washed with ether, gives the addition-product in pure condition. A small amount of the substance may be obtained from the mother-liquor by concentration. The yield is about 80 per cent. of the theoretical. For analysis it was recrystallized from alcohol and dried at 100°.

I. 0.2251 gram substance gave 0.4572 gram CO_2, and 0.0914 gram H_2O.

II. 0.3272 gram substance gave 44.5 cc. N at 13° C. and 765.5° mm.

	Theory for $C_6H_5-N_3C_2(COOCH_3)_2$.	Found.
C	55.17	55.39
H	4.21	4.52
N	16.09	16.18

The product forms white needles, that melt without decomposition at 127°–128°. It is insoluble in water, sparingly in carbon tetrachloride and ether in the cold, and has neutral properties.

To obtain the acid corresponding to this ester, a mixture of 24 grams ester, 19.2 grams potassium hydroxide, and 60 grams 70 per cent. alcohol, were heated four hours on a water-bath, the solution concentrated, and the acid precipitated by a mineral acid. After several crystallizations from water the product was in pure condition.

I. 0.1852 gram substance, dried at 100°, gave 0.3499 gram CO_2, and 0.0547 gram H_2O.

vacuum, as otherwise it may contain aniline, which it is difficult to separate by distillation. We found the following directions gave the best yield of acetylenedicarboxylic ester. 25 grams acid, 70 grams methyl alcohol, and 4 grams sulphuric acid were heated for 45 minutes in a water-bath with an inverted cooler. The product was heated with slanting cooler as long as alcohol passed over readily, then thrown into water and the mixture extracted with ether. The ethereal solution was extracted with sodium carbonate, which removed considerable acid-ester and which may be used for the preparation of neutral ester. The neutral ester is fractionated in a vacuum several times to remove higher boiling products.

II. 0.2757 gram substance, dried at 100°, gave 43.8 cc. N at 15° C. and 748 mm.

	Theory for $C_6H_3N_3C_3(COOH)_3$.	Found.
C	51.50	51.53
H	3.00	3.27
N	18.03	18.31

The acid crystallizes from water in long, prismatic needles that resemble those of phthalic anhydride, and melts with decomposition at 149°–150°. It is moderately soluble in cold water, more easily in alcohol, and readily in hot water.

A neutral solution of the potassium salt shows the following behavior towards metallic salts:

$BaCl_2$: On mixing the solutions a white crystalline precipitate of the barium salt is deposited, which consists of short plates, sparingly soluble in cold water.

$MgCl_2$: No precipitate.

$CuSO_4$: No precipitate.

$CdSO_4$: Slight precipitate of colorless groups of crystals.

$Pb(NO_3)_2$: White, crystalline precipitate.

Fe_2Cl_6: Yellowish precipitate with crystalline structure.

The silver and calcium salts were analyzed.

Silver Salt.—Fine, white needles, that are sparingly soluble in cold water.

I. 0.6721 gram, air-dried, silver salt lost 0.0290 gram H_2O at 100°, and could not be heated higher without decomposition.

II. 0.6431 gram salt, dried at 100°, gave 0.3106 gram silver.

	Theory for $C_{10}N_3O_4H_3Ag_2.H_2O$.	Theory for $C_{10}N_3O_4H_3Ag_2$.	Found.
H_2O	3.87	....	4.31
Ag	....	48.59	48.29

Calcium Salt.—White, truncated prisms, that are grouped in star-like forms, and are moderately soluble in cold water.

I. 0.4000 gram air-dried salt lost 0.099 gram water at 135°.

II. 0.3010 gram salt, dried at 135°, gave 0.1515 gram $CaSO_4$.

	Theory for $C_{10}N_3O_4H_3Ca.5H_2O$.	Theory for $C_{10}N_3O_4H_3Ca$.	Found.
H_2O	24.93	....	24.75
Ca	....	14.75	14.77

The acid melts with partial decomposition, and with evolution of carbon dioxide. To study this reaction a portion of the acid was heated to 150° in a metal bath as long as carbon dioxide came off, and the residue, which solidified on cooling, together with the portion that had sublimed into the upper part of the flask, was extracted with aqueous sodium carbonate, and the residue then crystallized three times from hot water. An analysis of this product gave the following figures:

0.1635 gram vacuum-dried substance gave 0.3975 gram CO_2, and 0.0770 gram H_2O.

	Theory for $C_5H_5N_3C_3H_2$.	Found.
C	66.23	66.29
H	4.82	5.22

The substance forms white crystals, that are moderately soluble in cold, readily in hot, water or alcohol, and melt, without decomposition, at 55°–56°. It volatilizes with steam with a pleasant, aromatic odor. In the decomposition of the dibasic acid both of the carboxyls have been removed, and the product therefore has not acidic properties; but, on the other hand, it shows the properties of an imidodiazol, inasmuch as it dissolves in hydrochloric acid, and is not precipitated by water from this solution. The basic properties, however, are so slightly developed that the hydrochlorate only exists in solution, and evaporation of this solution in a vacuum leaves the original substance. A double salt with platinic chloride is obtained by adding the chloride to the hydrochloric acid solution of the compound, and washing the precipitate with dilute hydrochloric acid. It forms long, prismatic needles, which, after drying first in a vacuum, then at 100°, were analyzed:

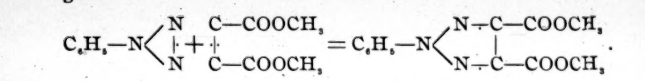
I. 0.5950 gram vacuum-dried salt lost 0.0115 gram H_2O at 100°.

II. 0.5835 gram salt, dried at 100°, gave 0.1640 gram Pt.

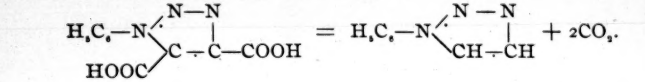
	Theory for $(C_5H_5N_3)_2PtCl_6.H_2O$.	Theory for $(C_5H_5N_3)_2PtCl_6$.	Found.
H_2O	2.52	....	1.93
Pt	....	27.84	28.01

The dibasic acid described above is isomeric with the

n-phenylosotriazoldicarboxylic acid of Pechmann.[1] An ester of this acid would be formed in the reaction of phenylazimide on acetylenedicarboxylic ester, by assuming that the addition occurs through disruption of the unsaturated nitrogen:



A comparison of the properties of Pechmann's with those of our acid shows conclusively that they are not identical, and there are therefore only the two constitutions already considered that are possible for our product. Since the single-chain triazol constitution is at present the more probable, we shall consider our substances as derivatives of this body. According to this conception the dibasic acid may be called *n*-phenyl-1,2-imidodiazoldicarboxylic acid,[2] and its decomposition by heat may be represented as follows:



The basic compound is therefore *n*-phenyl-1,2-imidodiazol, and it shows the stability towards bases and acids which characterizes the imidodiazol ring. Even towards oxidizing agents it shows itself as a very stable substance. A portion of the compound was heated for ten hours with an excess of potassium permanganate, and, after the excess of permanganate was removed by addition of sufficient alcohol, the liquid was found to contain considerable unchanged substance, besides oxalic acid and a small amount of a second acid, which was not further examined.

Conversion of n-Phenylimido-1,2-diazoldicarboxylic acid into Imido-1,2-diazoldicarboxylic Acid.

We first attempted to remove the phenyl in the dibasic acid by oxidation. A solution of 2 grams of acid, 2 grams potas-

[1] Ann. Chem. (Liebig), **262**, 311.

[2] Of the various nomenclatures suggested for this and analogous classes of substances, that of deriving them from the radicals, 1-azole, —CH=CH—CH=N—, or from 2-azole, —CH . CH—N . CH—, seems the simplest.

sium hydroxide, 10.8 grams potassium permanganate (equivalent to 12 atoms oxygen to 1 molecule of acid) and 60 grams water was boiled six hours, when about 0.1 of the permanganate was still unacted on. The excess of oxidizing agent was removed by alcohol, and the liquid, after filtration, concentrated, acidified with acetic acid, and calcium acetate added. After filtration from the calcium oxalate, the filtrate was acidified with nitric acid, and a concentrated solution of silver nitrate added, when a precipitate of a silver salt was deposited. This salt was treated in the cold with concentrated chlorhydric acid, an equal volume of water then added, and the mixture heated and filtered from silver chloride. On cooling a crystalline substance separated, which, after several crystallizations from dilute chlorhydric acid, melted at 146°–147°, and had the properties of the original dibasic acid. Its identity with the acid was further confirmed by decomposing a small quantity of the substance at 150°, when the basic phenylimidodiazol, melting at 55°–56°, was obtained. According to this result the dibasic acid is oxidized in alkaline solution with difficulty, with formation of oxalic acid.

Baltzer and Pechmann[1] succeeded in obtaining imido-1,4-diazolcarboxylic acid (osotriazolcarboxylic acid) by oxidation of amido-*n*-phenylimido-1,4-diazolcarboxylic acid; the introduction of the amido group rendering the benzene-nucleus easily susceptible to oxidation, and we adopted this method to replace phenyl by hydrogen in our dibasic acid.

We first attempted to introduce a nitro group into the phenyl of the compound by direct treatment with a mixture of fuming nitric and concentrated sulphuric acids, varying the conditions of temperature and time, and, although a reaction took place, the yield of nitro product obtained was inconsiderable. The product formed in this way was crystalline, sparingly soluble in water, and melted at 204°.

We then attempted to prepare the ester of the nitro acid by addition of nitrophenylazimide to acetylenedicarboxylic ester, and with better success. When we began these experiments there were two methods known to prepare nitrophenylazimide, and preliminary experiments induced us to

[1] Ann. Chem. (Liebig), **262**, 314.

prepare the product by direct nitration.[1] Although we varied the conditions of the nitration we were not able to obtain more than 44 per cent. of the weight of phenylazimide in a pure nitro product; but as this is a somewhat better yield than had been previously obtained, we give the conditions observed in the nitration. To a well-cooled quantity of phenylazimide a cold mixture of twice the weight of fuming nitric acid and an equal weight of concentrated sulphuric acid was added in small portions at a time, the flask being well shaken after each addition, and care being taken to prevent the temperature of the contents of the flask from rising above 0° during the operation. The product was allowed to stand in ice for an hour, then poured into water, and steamed as long as the nitro product passed over. The crude product melted from 57°–66°, but by several crystallizations from alcohol it became constant at 72°–73°. Subsequently Noelting and Michel[2] published an excellent and much more convenient method of preparing this substance from *p*-nitrodiazobenzene sulphate and hydrazine, and we used their method to obtain the substance.

A solution of nitrophenylazimide and acetylenedicarboxylic methyl ester, in molecular proportions, in double the weight of dry benzene, was heated, in an open flask connected with an inverted cooler, for eight hours, and, after cooling, the light-brown precipitate was filtered under pressure and washed with a little dry benzene. The product thus obtained was pure, as shown by analysis:

I. 0.2020 gram substance, dried at 100°, gave 0.3479 gram CO_2, and 0.0605 gram H_2O.

II. 0.1835 gram substance, dried at 100°, gave 28.7 cc. N at 13° C. and 750 mm. pressure.

	Theory for $C_8H_4\langle^{NO_2}_{N_2C_2(COOCH_3)_2}$.	Found.
C	47.05	46.97
H	3.26	3.31
N	18.30	18.21

[1] Culmann and Gasiorowski: J. prakt. Chem., **40**, 116.
[2] Ber. d. chem. Ges., **26**, 90.

p-Nitro-*n*-phenylimido-1,2-diazoldicarboxylic methyl ester crystallizes from alcohol in needles, that melt at 117°–118°. It is moderately soluble in cold, easily in hot, benzene and hot alcohol; insoluble in water.

In saponifying this ester the use of alcoholic potash must be avoided, as complex decomposition-products are formed, probably in consequence of a partial reduction of the nitro group. Even when aqueous potash is used, certain precautions are necessary. The best results were obtained by heating 3 grams of ester, 2.7 grams caustic potash, and 90 grams water for an hour and a half, and testing at the end of that time whether any unchanged ester separated from a small portion of the liquid on cooling. If not, the solution was allowed to cool, and about one-half its volume of moderately strong chlorhydric acid added to it. On rubbing the sides of the vessel crystals separated, which were filtered and washed with a little water. These crystals left a trace of mineral matter when ignited; they were dissolved in a small amount of warm water, and an equal volume of hydrochloric acid added. The product deposited on cooling was crystallized from water and analyzed.

I. 0.1830 gram of substance, dried at 100° in a vacuum, gave 32.4 cc. N at 19°.5 C. and 764.5 mm.

II. 0.2336 gram of substance, dried at 100° in a vacuum, gave 43 cc. N at 19° C. and 754.5 mm.[1]

	Theory for $C_6H_4\langle^{NO_2}_{N_2C_2(COOH)_2}$	Found. I.	II.
N	20.14	20.42	20.95

The acid crystallizes from water in almost white plates and needles, the latter gradually passing over into the former on standing. It is moderately soluble in cold, easily in hot, water, very slightly in chlorhydric acid, and melts with decomposition at 162°–163°. To reduce the nitro acid it was gradually introduced (3.5 grams) into a warm solution of 9 grams hydrated stannous chloride in 15 grams concentrated chlorhydric acid, a fresh portion of the substance being

[1] In this determination a product was used that had lost a little carbon dioxide in treatment with too strong chlorhydric acid.

added only after reduction had taken place. On cooling and stirring the liquid a grayish salt separated, which was filtered and washed with concentrated chlorhydric acid. The salt was allowed to stand for an hour with an excess of ammonia, then filtered, the precipitate washed with water, and to the filtrate, after heating on a water-bath to drive off part of the free ammonia present, acetic acid was added. The straw-colored precipitate was filtered and washed. As it left a slight mineral residue on ignition, an attempt was made to remove the impurity by crystallizing from water. About one-half of the substance went into solution, but the dissolved part did not crystallize out when the solution became cold. On concentrating, straw-colored filaments and few prismatic crystals separated, which contained mineral matter, and when the concentrated solution was treated with glacial acetic acid in excess, a difficultly soluble precipitate was deposited, which is identical with the part of the original substance that did not dissolve in water, and which consisted of prismatic crystals. These crystals, being free of mineral matter, were recrystallized from considerable hot water, and analyzed.

0.1683 gram substance, dried at 100°, gave 34.2 cc. N at 21° C. and 759 mm.

	Theory for $C_6H_4\langle^{NH_2}_{N_2C_2(COOH)_2}$	Found.
N	22.58	23.04

Amido-*n*-phenyl-1,2-diazoldicarboxylic acid separates from hot water in thick, prismatic crystals, that are quite insoluble in cold and only moderately in boiling water. The melting-point varies somewhat according to the rapidity of heating, being usually at 218°–219°, but it may melt as low as 214°–215° or as high as 225°–226°, according to the conditions. The substance shows acid and basic properties, dissolving in alkalies and mineral acids, but not, as is evident from its preparation, in acetic acid. We first endeavored to obtain imidodiazoldicarboxylic acid from the imido acid by following the directions given by Baltzer and Pechmann.[1] One gram of acid was dissolved in a solution of 1.4 grams caustic potash in 60 grams

[1] Ann. Chem. (Liebig), **262**, 317.

water, and a saturated solution of potassium permanganate added, in small portions at a time, until no further oxidation took place in the cold, when it was continued for an hour in a hot water-bath. During the operation the solution was kept alkaline by addition of caustic potash. The solution was decolorized by alcohol, filtered from manganese dioxide. The filtrate was slightly acidified by acetic acid, filtered from a gelatinous orange-colored substance, and the oxalic acid formed in the oxidation precipitated by calcium chloride. The filtrate from the calcium oxalate was treated with cupric acetate, when a voluminous, blue precipitate was deposited, which, after washing, was suspended in water, decomposed by hydrogen sulphide, and the filtrate from copper sulphide concentrated when white crystals separated on cooling. This substance contained mineral matter, which could not be removed by crystallization from chlorhydric acid, and the yield of it obtained was so small that this method of oxidation and treatment was given up. A more satisfactory result was obtained by following the method used by Bladin[1] in the oxidation of azimidotoluene. Portions of 3 grams of amido acid were dissolved in 12 grams of a 10 per cent. solution of sodium hydrate, and a warm concentrated solution of permanganate added to the solution, until no further oxidation took place. The excess of oxidizing agent was removed by alcohol, and the manganese dioxide separated by filtration. As the dioxide retains some of the oxidation-product it was extracted with boiling water, and the filtrate from it added to the first filtrate. The pale green solution was made slightly acid with acetic acid, concentrated to a small bulk, and an excess of acetic acid added. The orange-colored precipitate was filtered, and a considerable excess of nitric acid, then a solution of silver nitrate added to the filtrate. A yellowish precipitate of silver salt was deposited, which was decomposed by warming with an excess of dilute chlorhydric acid, and the filtrate from silver chloride concentrated, when a white crystalline substance separated on cooling. The yield was small, only 1 gram of acid from 6 grams of amido compound. For analysis it was recrystallized.

[1] Ber. d. chem. Ges., **26**, 545, 2736.

0.1618 gram acid, dried at 100°, gave 0.1829 gram CO_2, and 0.0279 gram H_2O.

	Theory for $N_2HC_2(COOH)_3$.	Found.
C	30.57	30.82
H	1.91	1.91

The acid forms prismatic crystals, that melt, with decomposition and evolution of carbon dioxide, at 200°–201°. It is easily soluble in hot water and cold acetic ester, also in hot strong chlorhydric acid; only slightly soluble in hot chloroform and carbon tetrachloride.

A portion of the acid was neutralized by ammonia, and gave the following tests:

$AgNO_3$: Voluminous, pale-yellow precipitate, almost insoluble in nitric acid.

$BaCl_2$: Heavy white crystalline powder, without discernible crystalline form, but on standing it gradually goes over into tufts of acicular crystals.

$CaCl_2$: White groups of spear-like plates that are difficultly soluble in water.

$CuSO_4$: Light-blue precipitate of granular crystals that are easily soluble in mineral acids and ammonia.

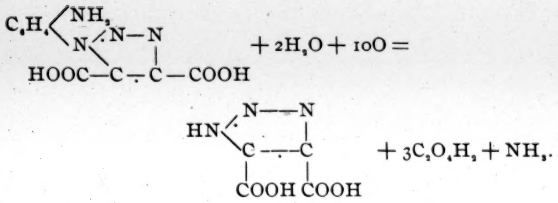
The acid potassium salt was made by dissolving the acid in a slight excess of caustic potash and then adding dilute chlorhydric acid until the solution gave a slightly acid reaction for the mineral acid, when it separated as microscopic needles, that are moderately soluble in cold and easily in hot water. The salt contains one molecule of water of crystallization.

0.3126 gram air-dried salt lost 0.0261 gram water at 100°.

	Theory for $C_4N_2O_4H_3K.H_2O$.	Found.
H_2O	8.45	8.03

A comparison of the properties of this acid with the triazoldicarboxylic acid obtained by Bladin[1] by the oxidation of azimidotoluene leaves no doubt that the substances are identical, and, assuming the open five-membered ring constitution for our imidodiazol derivatives, the formation of the acid may be represented as follows:

[1] Ber. d. chem. Ges., **26**, 545 and 2736.



In the preparation of imidodiazoldicarboxylic acid, we mentioned a voluminous substance which was precipitated when acetic acid is added to the oxidized product. The substance, which is formed in considerable amount, as we obtained 1.4 grams of it in oxidizing 3 grams amido acid, forms an orange-red body, that does not melt when heated, but swells up and turns to a black mass, and heated higher it burns leaving a mineral ash. To free it from mineral matter it was digested for a half hour with moderately strong hydrochloric acid, the insoluble part washed with water, and crystallized from a considerable amount of hot water. It forms orange-red, granular crystals, that begin to darken at 326°, and melts at 328°–330°, with decomposition. The following analysis does not agree with any simple decomposition-product of the amido acid, and want of time prevented a further investigation of the substance.

0.1644 gram substance, dried at 100°, gave 0.2738 gram CO_2 and 0.0453 gram H_2O.

C	45.42
H	3.06

Nitrophenylimidodiazoldicarboxylic acid decomposes, with evolution of carbon dioxide, more easily than the mother-acid, and a few minutes' heating at 160° suffices to effect complete decomposition. The dark-brown residue was extracted with hot alcohol, and, as the new substance is only slightly soluble in the hot solvent, it was found advisable to filter the alcohol while hot, and, after cooling and removal of the precipitate by filtration, again extract with the same alcohol, repeating the operation until all the residue was used up. A

treatment with bone-black, and a second crystallization from the alcohol, gave a pure substance.

0.2543 gram of substance, dried at 100°, gave 63.4 cc. N at 13°.5 C. and 767.5 mm.

	Theory for $C_6H_4\langle^{NO_2}_{N_3C_3H_3}$	Found.
N	29.47	29.67

p-Nitro-*n*-phenyl-1-2-imidodiazol forms pale-yellow, granular crystals, that melt at 203°–204°. It is difficultly soluble in water, benzene, and alcohol, even in the heat; easily soluble in acetic ester, and hot methyl alcohol. The substance has neutral properties, the introduction of the nitro group having neutralized the slight basic properties of *n*-phenylimidodiazol.

To reduce the nitro group in this compound it was warmed with concentrated hydrochloric acid and tin until complete solution ensued, and the grayish, crystalline tin double salt that separated on cooling, dissolved in hot water, and hydrogen sulphide passed through the warm solution until all the tin was precipitated. On evaporation of the filtrate to dryness in a water-bath, extraction of the residue by water, and addition of an excess of caustic potash to the filtered solution, the new base was precipitated. The yield was not satisfactory, and we found that a somewhat better result was obtained by using stannous chloride as reducer. The substance was warmed with dilute hydrochloric acid, and an amount of stannous chloride slightly in excess of the theory until reduction had taken place. Water was added to the solution, and the liquid treated as already described. The base was obtained pure by two crystallizations from hot water.

I. 0.1520 gram substance, dried at 100° in a vacuum, gave 0.3352 gram CO_2, and 0.0708 gram H_2O.

II. 0.2071 gram substance, dried at 100° in a vacuum, gave 64.5 cc. N at 23°.5 C., and 774.5 mm.

	Theory for $C_6H_4\langle^{NH_2}_{N_3C_3H_3}$	Found.
C	60.00	60.16
H	5.00	5.18
N	35.00	35.60

The substance crystallizes in pearly flakes, that melt at 138°–139°. It is easily soluble in hot water and hot benzene, slightly in hot alcohol and acetic ester. With the ordinary mineral acids it gives salts, which are soluble in water. A small quantity of the base was dissolved in hot water, and, after addition of some alkali, an excess of permanganate added. On working up the solution, as already described for the amidodicarboxylic acid, a crystalline substance and oxalic acid were obtained, but the formation of imidodiazol, which is a liquid and a basic substance, was not noticed.

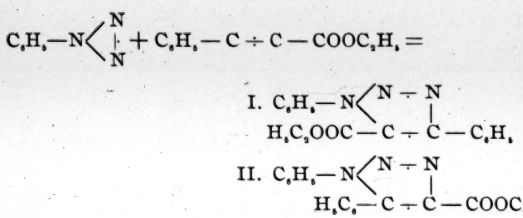
Addition of Phenylazimide to Phenylpropiolic Ethylester.

In order to ascertain whether the reaction we have described in this paper is applicable to the esters of monobasic acids, we examined the behavior of phenylazimide towards ethyl phenylpropiolate. The addition does not take place as easily as when acetylenecarboxylic ester is used, and the operation is best carried out in a sealed tube at 100°. Five grams of phenylazimide, 7.5 grams ester, and 15 grams dry ether, were heated for sixteen hours, and the tube, when cold, opened under a slight pressure. On standing a short time after opening, the liquid in the tube deposited a crystalline substance, which was separated, washed with benzene, and recrystallized twice from a mixture of three parts benzine and one part benzene. A small amount of addition-product may be obtained by heating the mother-liquor again. The substance gave the following figures for nitrogen:

0.1715 gram substance, dried at 100°, gave 21.8 cc. N at 9.5° C., and 733.5 mm.

	Theory for $C_6H_5-N_3C_3\begin{matrix}C_6H_5\\COOC_2H_5\end{matrix}$	Found.
N	14.34	14.72

The product crystallizes in needles that melt at 134°–135°, and are freely soluble in benzene and acetic ester in the cold, very soluble in the heat; but only sparingly soluble in benzine. This addition may proceed in two different ways, forming isomeric products:



The data for determining with certainty which of these constitutions should be assigned to our substance, are not known, although constitution II. is the more probable. The ester is easily saponified by boiling with alcoholic potash for a short time. On evaporation of the alcohol, and acidifying with chlorhydric acid, the acid is precipitated. By crystallizing twice from dilute alcohol a pure product was obtained.

I. 0.196 gram acid, dried at 100°, gave 0.488 gram CO_2, and 0.080 gram H_2O.

II. 0.220 gram acid, dried at 100°, gave 30 cc. N at 11° C. and 745 mm.

	Theory for $C_6H_5-N_2C_2\begin{matrix}C_6H_5\\COOH\end{matrix}$	Found.
C	67.92	67.85
H	4.15	4.48
N	15.85	15.93

n-Phenylimido-phenyl-1,2-diazolcarboxylic acid is a crystalline, white substance that melts at 183°. It is slightly soluble in water, more easily in alcohol.

A neutral solution of the ammonium salt gives the following reactions:

$BaCl_2$: White, amorphous precipitate.

$MgSO_4$: The mixture remains clear for several minutes, then round groups of needles separate.

$Pb(NO_3)_2$: White, amorphous precipitate.

$CdSO_4$: White, amorphous precipitate.

The silver salt forms a white, amorphous substance, which is difficultly soluble in cold water.

0.559 gram salt, dried in a vacuum, gave 0.161 gram Ag.

	Theory for $C_{14}N_3H_{16}COOAg$.	Found.
Ag	29.03	28.80

The copper salt is precipitated as an amorphous mass, that soon turns to groups of truncated, slender prisms.

0.2535 gram salt, dried in vacuum, gave 0.0350 gram CuO.

	Theory for $(C_{14}N_3H_{16}COO)_2Cu$.	Found.
Cu	10.70	11.02

Since the fatty monobasic acetylene acids add negative atoms more readily than phenylpropiolic acid, there can be no doubt that the addition of substituted azimides to esters of the acetylenecarboxylic acids to form imidodiazol derivatives is a general reaction.

TUFTS COLLEGE, MASS.

Contributions from the Chemical Laboratory of Harvard College.

CVI. — ON THE OXIDE OF DICHLORMETHOXYQUINONEDIBENZOYLMETHYLACETAL.[1]

BY C. LORING JACKSON AND H. A. TORREY.

A paper on the acetals derived from substituted quinones published by H. S. Grindley and one of us in 1895, contained a description[2] of a substance made by the action of sulphuric acid on the dichlordimethoxyquinonedibenzoyldimethylacetal, which had the formula, $C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2O$, and which was called then the oxide of dichlordimethoxyhydroquinone dibenzoate—a name which the better knowledge of its constitution obtained from the work described in this paper makes it necessary for us to change to oxide of dichlormethoxyquinonedibenzoylmethylacetal.

As it seemed probable that the atom of oxygen in this substance was attached to two of the carbon atoms of the benzol ring, we decided to continue the study of it, and we describe the results of our work in this paper. In the preceding paper nothing had been done with this body beyond establishing its composition and that of the corresponding ethyl compound,

[1] Presented to the American Academy of Arts and Sciences, May 12, 1897. The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy, by H. A. Torrey.

[2] This JOURNAL, 17, 644.

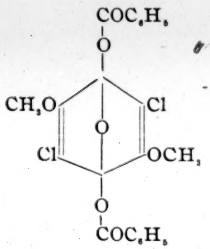
and the preparation and partial study of a reduction-product obtained from the ethyl oxide by the action of hydriodic acid.

In taking up again the study of the oxide the first point to be determined was whether the atom of oxygen is attached to one atom of carbon or to two. In the former case the substance must be either a ketone or a phenol. In writing the formula of this substance on the supposition that it is a ketone, it is necessary to assume such improbable intramolecular transformations that we felt inclined to reject the ketone formula on this ground alone; and this theoretical deduction was confirmed by the behavior of the substance. Hydroxylamine does not act on the body; but with phenylhydrazine products are obtained, to which we have devoted much attention with little result, because they are so unstable. They seem to resemble the isoamylamine compounds described later, and, if this is the case, tell against a ketone formula for the substance. This evidence, therefore, so far as it goes, is unfavorable to the ketone formula, but not conclusive against it. The action of a hot solution of sodic hydrate on our substance converted it into the sodium salt of chloranilic acid, and this result cannot be brought into harmony with a ketone formula, for in that case the sodic hydrate must have converted the ketone group C=O into a phenol group C—OH. The ketone attachment of the oxygen must, therefore, be rejected.

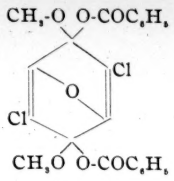
We have not succeeded in constructing any formula for our substance with the oxygen present in a hydroxyl group, as this would give 7 substituting radicals to be arranged upon the benzol ring; and we may add that the existence of a hydroxyl group is inadmissible on experimental grounds, since cold sodic hydrate has no action upon the substance.

After we had thus proved that the oxygen is not attached to a single atom of carbon, a molecular weight determination was made, which showed that the body was derived from only one molecule of the substituted quinone. We next considered the different ways in which the atom of oxygen could be attached to 2 atoms of carbon, and this led to 4 possible formulas for the substance:

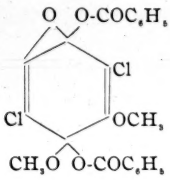
I.



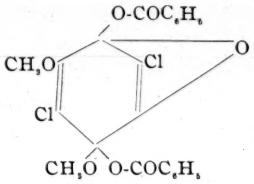
II.



III.



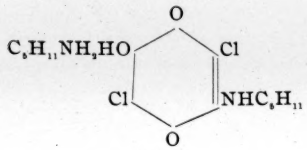
IV.



In formulas I. and II. the attachment is to two atoms of carbon in the para position, which in I. are the quinone atoms of carbon, in II. those which are attached to the hydroxyls in chloranilic acid. Formula III. represents the oxygen attached to 2 atoms of carbon in the ortho position; and formula IV. shows a meta attachment. Of the formulas we considered I. or II. the most probable, and devoted ourselves at first to the study of these.

The conversion of the substance into chloranilic acid by the action of hot sodic hydrate can be easily explained by all four of these formulas, and therefore gives no aid in distinguishing between them.

Isoamylamine converts the oxide into the isoamylamine salt of oxydichlorisoamylamidoquinone, which has the following formula:

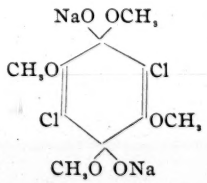


In forming this substance from a body having formula I., it is necessary that the two methoxy groups should be acted on differently by the isoamylamine, since one of them is replaced by the isoamylamido group ($C_5H_{11}NH$), and the other converted into the phenol salt group ($C_5H_{11}NH_2HO$). Such an action would be highly improbable theoretically, as these two methoxy groups are symmetrically disposed in this formula; and it is proved to be impossible by our study of the action of isoamylamine on the similarly constituted dichlordimethoxyquinonedimethyldibenzoylacetal,

$$C_6Cl_2(OCH_3)_2(OCH_3)_2(OCOC_6H_5)_2,$$

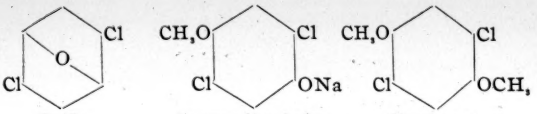
which was converted by it into dichlordiisoamylamidoquinone, $C_6Cl_2(NHC_5H_{11})_2O_2$. Formula I., therefore, is not in harmony with these observations, and must be rejected. Formulas II., III., and IV. can be easily brought into harmony with the results of the experiments with isoamylamine, as will be shown later.

Sodic methylate converted the oxide into the sodium salt of the dichlordimethoxyquinonedimethylhemiacetal, which has the following formula:



In deriving this compound from a substance having formula II., the atom of oxygen must take up a molecule of sodic

methylate, thus producing the intermediate body of these formulas :[1]

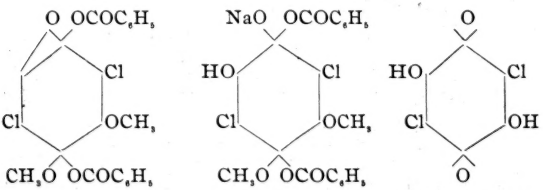


Oxide. Intermediate body. Hemiacetal.

And then we must assume that the ONa of this body is converted into the OCH_3 of the hemiacetal by sodic methylate, an assumption which cannot be justified by any analogy, so that formula II. must also be rejected.[2]

There remain only formulas III. and IV., the unsymmetrical structure of which made us at first think them highly improbable ; as a matter of fact, however, both of them explain in a satisfactory manner all the observations. This we will show only with formula III., since formula IV. would behave in a similar manner in every case.

The conversion of the oxide into chloranilic acid by sodic hydrate would take place in three stages ; first, the addition of 1 molecule of sodic hydrate to the atom of oxygen, thus :



Oxide. Intermediate product. Chloranilic Acid.

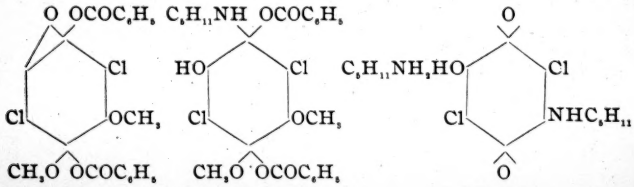
second, the saponification of the acetal groups to the quinone ;

[1] In these formulas the radicals in the quinone positions have been left out for the sake of simplicity. They offer no difficulties, as will be shown later.

[2] It is perhaps worth while to state that the conversion of the hypothetical intermediate body into the hemiacetal could be brought about by splitting off sodic benzoate, thus forming a new oxide, which afterward might react with the sodic methylate ; but, as this new oxide must have the conformation of either formula III. or IV., it does not seem worth while to bring this strained hypothesis forward as a support for formula II.

and third, the saponification of the methoxy group to a hydroxyl.[1]

The formation of the isoamylamine salt of oxydichlorisoamylamidoquinone by the action of isoamylamine on the oxide would begin by the addition of one molecule of isoamylamine, forming the intermediate product, which would then



Oxide. Intermediate product. Product.

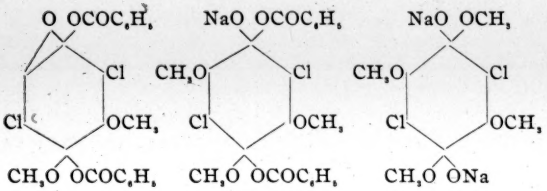
be followed by the conversion of the acetal groups to the quinone, the replacement of the methoxy group by the isoamylamido group $C_5H_{11}NH$, and the addition of a molecule of isoamylamine to the hydroxyl. The two steps in this conversion which might be regarded as doubtful are the conversion of the acetal to the quinone by isoamylamine, and the replacement of the methoxy by the isoamylamido group. Fortunately, we have been able to remove all doubt about both these steps by acting on the dichlordimethoxyquinonedimethyldibenzoylacetal,

$$C_6Cl_2(CH_3O)_2(CH_3O)_2(OCOC_6H_5)_2,$$

with isoamylamine, when it was converted into dichlordiisoamylamidoquinone, $C_6Cl_2(C_5H_{11}NH)_2O_2$.

The formation of the sodium salt of the dimethylhemiacetal by the action of sodic methylate on the oxide is explained in a similar way :

[1] That such methoxy groups on a quinone ring are saponified by sodic hydrate has been shown by the experiments of H. S. Grindley and one of us. (This JOURNAL, 17, 606.) In this respect they resemble those in picric ether or trinitrophloroglucine ether much more than those in anisol.



Oxide. Addition product. Hemiacetal.

The formation of the intermediate addition-product being followed by conversion into a quinone, which then takes up 2 molecules of sodic methylate to form the hemiacetal.

The only other derivative of the oxide known is the reduction-product[1] obtained by Grindley and one of us by the action of hydriodic acid. This substance gave upon analysis the formula $C_6Cl_2OC_6H_4OH(OCOC_6H_5)_2$, but has not yet been studied sufficiently to determine its constitution with certainty. We shall therefore content ourselves with saying that a substance with the formula given above could be easily derived from the oxide with the ortho attachment by the action of hydriodic acid.

In the foregoing discussion of the formulas of the oxide, the arguments were based in large part among the product obtained from it by the action of isoamylamine, and it is necessary, therefore, here to give our proofs of the constitution of this body. Its analysis led to the formula

$$C_6Cl_2(C_5H_{11}NH)(C_5H_{11}NH_2HO)O_2,$$

which represents an isoamylamine salt of a phenol, and this view was confirmed by the following observations: sodic hydrate set free isoamylamine from it; with hydrochloric acid a substance was obtained of the formula $C_6Cl_2(C_5H_{11}NH)HOO_2$, and melting at 188°; argentic nitrate converted it into

$$C_6Cl_2(C_5H_{11}NH)AgOO_2,$$

and we have also made the corresponding barium salt. That it was a quinone was shown by its dark color and its conversion into a colorless product by reduction. For the sake of com-

[1] This JOURNAL, 17, 641.

parison with this body we made the dichlordiisoamylamidoquinone, $C_6Cl_2(C_5H_{11}NH)_2O_2$, by the action of isoamylamine on chloranil; it melted at 224° to 225°; and also the isoamylamine salt of chloranilic acid, $C_6Cl_2(OHH_2NC_5H_{11})_2O_2$, both of which differed entirely in properties from the product made from the oxide.

The oxide when treated with diisoamylamine gave a compound corresponding to that from isoamylamine,

$$C_6Cl_2(C_5H_{11})_2N(C_5H_{11})_2NHHOO_2,$$

melting at 168°–169°. With chloranil, diisoamylamine gave

$$C_6Cl_2((C_5H_{11})_2N)_2O_2.$$

In looking for actions analogous to those just described, we are obliged to resort to the fat series, as no oxide similar to ours is known in the aromatic series, the nearest approach to it being cineol according to the formula ascribed to it by Brühl, in which, however, the oxygen spans the benzol ring in the para position. In the fat series ethylene oxide shows a structure similar to that of our oxide, as its atom of oxygen is attached to two adjacent atoms of carbon; and in its behavior with various reagents we find a marked similarity to the reactions of our oxide. Thus its conversion into glycol by the action of water corresponds to the formation of chloranilic acid by sodic hydrate, and with ammonia the ethylene oxide gives, among other products, an amino-alcohol,

$$HOCH_2CH_2NH_2,$$

analogous to the intermediate product which must be formed by the action of isoamylamine on our oxide. On the other hand, we have not been able to find any case in which a fat oxide belonging to another than the α series shows these reactions, and this, so far as it goes, throws the balance in favor of adopting the ortho attachment of the oxygen (formula III.) rather than the meta attachment (formula IV.) in our oxide.

The decision between formula III. (with the ortho attachment) and formula IV. (with the meta attachment) could not be founded on any study of the derivatives of the oxide, as both formulas would give the same products when the oxygen

bond was opened. We accordingly tried to solve the problem by the study of analogous substances, as follows: we exposed to the action of boiling sulphuric acid resorcine as an example of a substance with meta hydroxyls, and pyrocatechine (or some of its derivatives) as a substance with ortho hydroxyls, in the hope of obtaining an oxide similar to the one we have been studying, but in neither case was an oxide of this class formed. Resorcine under the action of boiling dilute sulphuric acid gave a body which we recognized by its properties as resorcine ether, formed by the union of 2 molecules of resorcine. The experiments with pyrocatechine and its derivatives, when the substance underwent any change, gave colored products, which were probably formed from a quinone. These experiments, therefore, threw no light upon the question.

From the discussion given above it appears that we cannot decide with certainty whether the oxygen in our oxide is in the ortho or meta position; we are of the opinion, however, that it has the ortho attachment, not only from the analogy between our oxide and ethylene oxide pointed out above, but also from the fact that the formation of anhydrides and similar couplings by two radicals in the meta position to each other are unknown, whereas these actions are among the most familiar characteristics of the ortho series.

We also describe tetrabromguaiacol, melting at 162°–163°, and tribromveratrol, melting at 86°–87°, which were made in connection with our work on the action of sulphuric acid on derivatives of pyrocatechine.

When we first undertook this work we devoted a great deal of time to the preparation of mixed acetals like the dichlordiethoxyquinonedimethyldibenzoylacetal, as we hoped by the saponification of these substances to be able to determine which of the formulas of the oxide was correct; but these experiments led to no satisfactory result, as the action of sodic methylate on dichlordiethoxyquinone, or of sodic ethylate on dichlordimethoxyquinone, produced mixtures from which the desired compounds could not be isolated. This is not surprising, as we found subsequently that the ethoxy groups could be replaced by methoxy groups, or the reverse, when

one of our compounds was treated with the sodic alcoholate containing the radical, which was not already attached to its quinone ring.[1]

The acetyl acetals corresponding to the benzoyl acetals have also been made by us, and have the following melting-points:

$C_6Cl_2(OCH_3)_2(OCH_3)_2(OCOCH_3)_2$, melting-point 177°–178°.
$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOCH_3)_2$, melting-point 120°–121°.

We also describe some experiments on the action of sodic alcoholates on quinone itself and on chloranil, which led to substances probably similar to the colored compounds obtained from nitro aromatic bodies by the action of sodic alcoholates by Lobry de Bruyn,[2] Victor Meyer,[3] and Ittner and one of us.[4] These experiments were abandoned after some progress had been made on account of the work of Astre[5] in the same field, and are described here only because they cannot be brought into harmony with the theory advanced by Astre to account for these substances. The discussion of this question will be found in the experimental part.

We also observed that an alkaline solution of sodic chloranilate was converted into iodoform by treatment with iodine.

Experimental Part.

Preparation of the Oxide of Dichlormethoxyquinonedibenzoylmethylacetal, $C_6Cl_2OCH_3O(CO_2C_6H_5)_2OCH_3$.

This preparation was carried on essentially in the manner described by Grindley and one of us in a previous paper,[6] but we think it best to describe the process again here, as in that paper it is not given continuously, but scattered through different paragraphs, and also because we have introduced a few improvements in the details.

To convert chloranil into dichlordiphenoxyquinone 50 grams of chloranil, previously converted to a fine powder by reduction to tetrachlorhydroquinone by sulphurous acid followed by

[1] Compare Gattermann and Ritschke, Ber. d. chem. Ges., **23**, 1738 (1890).
[2] Rec. Trav. Chim. Pays-Bas, **14**, 89.
[3] Ber. d. chem. Ges., **27**, 3153.
[4] This JOURNAL, **19**, 199.
[5] Compt. rend., **121**, 326, 530.
[6] This JOURNAL, **17**, 600.

oxidation with nitric acid,[1] were treated with a strong aqueous solution of potassic phenylate made from 50 grams of phenol and 25 grams of potassic hydrate. The product was washed thoroughly with water, then with alcohol, and finally with benzol or ether. It was not recrystallized.

The dichlordiphenoxyquinone was then converted into the dichlordimethoxydimethylhemiacetal by adding 20 grams of it in small portions at a time with constant agitation to the sodic methylate made from 5 grams of metallic sodium and 120 cc. of methyl alcohol. It was found best to carry on this reaction in a flask. The mixture was then warmed on the water-bath, and afterward allowed to stand for a short time to permit the separation of the sodium salt of the hemiacetal, which was sometimes hastened by the addition of a little ether. The salt collected on a filter was washed with ether and with a very little alcohol, or better a mixture of alcohol and ether.

The dibenzoylacetal was next made by treating 25 grams of the dry salt suspended in a small quantity of methyl alcohol with 22 grams of benzoyl chloride. The reaction was completed by warming the mixture for a short time on the water-bath. The product usually contained, in addition to the colorless dibenzoylacetal, a red substance, probably dichlordimethoxyquinone, which was most easily removed by treatment with warm sodic hydrate, as this reagent converted the red substance into sodic chloranilate, but did not act on the acetal. The chloranilate was then washed with hot water, leaving the acetal pure enough for our purposes.

The dry acetal was next saponified by heating it for fifteen or twenty minutes in a flask with a return-condenser with sulphuric acid of specific gravity 1.44. The contents of the flask were then allowed to cool, and after the addition of a little water the solid product was filtered out, and washed with hot water to remove the chloranilic acid always formed in the reaction. The white oxide left was then purified by one or two recrystallizations from chloroform and alcohol. The yield of oxide was a little under 80 per cent. of the amount which should be obtained from the acetal.

[1] This preliminary treatment is essential to the success of the process. We have not succeeded in getting a sufficiently fine powder by mechanical means.

The processes which are carried on in this preparation are represented by the following equations:

$$C_6Cl_4O_2 + 2NaOC_6H_5 = C_6Cl_2(OC_6H_5)_2O_2 + 2NaCl.$$

$$C_6Cl_2(OC_6H_5)_2O_2 + 4NaOCH_3 = C_6Cl_2(OCH_3)_2(ONa)_2(OCH_3)_2 + 2NaOC_6H_5.$$

$$C_6Cl_2(OCH_3)_2(ONa)_2(OCH_3)_2 + 2C_6H_5COCl = 2NaCl + C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2(OCH_3)_2.$$

$$C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2(OCH_3)_2 + H_2O = C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3 + 2CH_3OH.$$

Determination of the Molecular Weight of the Oxide.

This determination was made to find out whether the oxide was derived from one or more molecules of the benzoylacetal. The boiling-point method of Beckmann was used with benzol as the solvent, and the following results were obtained:

Solvent.	Substance.	Δ.	M.
17.08	0.4315	0.138°	489
17.05	0.6761	0.228°	465
17.02	0.9787	0.328°	468
		Mean,	474

The temperature error did not exceed 3 in the last decimal place.

Calculated molecular weight for $C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3$.	Found. Mean.
463	474

These results show that the oxygen atom does not bind together 2 benzol rings.

Action of Sodic Hydrate on the Oxide, $C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3$.

The oxide did not dissolve in a cold solution of sodic hydrate, but when the two substances were allowed to stand together for twenty hours, it was found that a small quantity of sodic chloranilate had separated out.

If on the other hand, the oxide was boiled with sodic hydrate, it was decomposed rapidly even when a dilute solution was used. 1.5 grams of the oxide were boiled for half an

hour with a solution of 5 grams of sodic hydrate in 60 cc. of water; at the end of this time the oxide had disappeared completely, and the liquid had taken on a dark purple color. It was filtered while still hot, and the filtrate on cooling deposited crystals, which looked like sodic chloranilate. To determine their composition they were collected on a filter, and, after washing with alcohol and a little water, recrystallized from hot water. The crystals were then dried over sulphuric acid, and finally at 110°–120°, when an analysis gave the following result:

0.1707 gram of the salt gave 0.0949 gram of sodic sulphate.

	Calculated for $C_6Cl_2(ONa)_2O_2$.	Found.
Sodium	18.18	18.02

The product was therefore sodic chloranilate.

Action of Sodic Methylate on the Methyl Oxide, $C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3$.

One gram of the oxide was added to a solution of sodic methylate made by the action of 0.2 gram of metallic sodium on 10 cc. of methyl alcohol. After heating the mixture for a short time on the water-bath the liquid became slightly yellow, and the oxide went into solution, but soon after a white substance was deposited, the quantity of which increased as the liquid cooled; at the same time the odor of methyl benzoate was observed. The product of the reaction was allowed to stand at ordinary temperatures for half an hour, after which the white precipitate was collected on a filter, and washed at first with methyl alcohol, in which it is only slightly soluble, and finally with ether. The washed precipitate was then dissolved in water, and the solution, after it had been filtered, acidified with dilute hydrochloric acid. The white flocculent precipitate formed by the acid was washed thoroughly with water, alcohol, and ether; and next redissolved in sodic hydrate, filtered, and reprecipitated with dilute hydrochloric acid. These solutions and reprecipitations were repeated several times until the precipitate was perfectly white.

The amorphous white substance thus obtained was very similar in appearance to a hemiacetal. It was dried and analyzed with the following result:

0.1368 gram of the substance gave, by the method of Carius, 0.1300 gram of argentic chloride.

	Calculated for $C_6Cl_2(OCH_3)_2(OH)_2(OCH_3)_2$.	Found.
Chlorine	23.59	23.48

This analysis indicates that the substance is the dichlordimethoxyquinonedimethylhemiacetal, and this view of its composition is confirmed by the following experiment. A small quantity of the substance was heated with dilute hydrochloric acid, when a red crystalline body was obtained melting in the crude state at 140°, after crystallization at 141°. This must therefore have been the dichlordimethoxyquinone whose melting-point is 141°–142°.

The hemiacetal could be formed from the oxide by the following reactions:

$$C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3 + NaOCH_3 =$$
$$C_6Cl_2(OCH_3)_2ONa(OCOC_6H_5)_2OCH_3 =$$
$$C_6H_5COONa + C_6H_5COOCH_3 + C_6Cl_2(OCH_3)_2O_2.$$

An odor of methyl benzoate was observed, as already stated.

$$C_6Cl_2(OCH_3)_2O_2 + 2NaOCH_3 =$$
$$C_6Cl_2(OCH_3)_2(ONa)_2(OCH_3)_2.$$

Action of Sodic Methylate on the Ethyl Oxide,
$C_6Cl_2(OC_2H_5)O(OCOC_6H_5)_2OC_2H_5$.

One gram of the ethyl oxide was added to a solution of sodic methylate made by the action of 0.2 gram of sodium on 12 cc. of methyl alcohol. The oxide went into solution at once, but after the solution had been heated on the steam-bath for a short time a white precipitate was thrown down, the amount of which was increased by the addition of ether. After purification by alternate precipitation by hydrochloric acid, and solution in sodic hydrate, as described in the preceding section, the substance was dried in a desiccator, and analyzed with the following result:

0.1527 gram of the free hemiacetal gave, by the method of Carius, 0.1456 gram of argentic chloride.

	Calculated for $C_6Cl_2(OCH_3)_2(OH)_2(OCH_3)_2$.	Found.
Chlorine	23.59	23.58

As the mixed ethyl methylhemiacetal, which would be expected here, contains 21.58 per cent. of chlorine, there can be no doubt that the product was the dimethylhemiacetal; and this view was confirmed by the following experiment: A small quantity of the substance was heated with dilute hydrochloric acid, when a red solid was formed which melted at 140°, and therefore was the dichlordimethoxyquinone. From these observations it follows that the behavior of the ethyl oxide with sodic methylate is the same as that of the methyl oxide, except that, in addition to the formation of the hemiacetal, the ethoxy groups have been replaced by methoxy groups.

After the work just described had shown that ethoxy groups in the ethyl oxide could be replaced by methoxy groups under the influence of sodic methylate, the following experiment was tried to see whether a similar change could be produced with the dichlordiethoxyquinone: 0.7 gram of this substance was treated with a solution of the sodic methylate made from 0.2 gram of sodium and 5 cc. of methyl alcohol; the hemiacetal formed was decomposed with dilute hydrochloric acid, and the red quinone obtained recrystallized from alcohol, and then from benzol, when it melted at 139°, showing that it was dichlordimethoxyquinone, and therefore that the methoxy groups had replaced the ethoxy groups in this case also, as was to be expected.

We next tried an experiment to see whether the reverse change could be brought about. One gram of the methyl oxide, $C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3$, was treated with a solution of sodic ethylate, and the hemiacetal formed decomposed with hydrochloric acid, when the crude quinone thus obtained melted at 100°–105°, and recrystallization did not raise the melting-point above 105°; it is, therefore, dichlordiethoxyquinone, which melts at 104°–105°, and the ethoxy group has replaced the methoxy group. These experiments make it probable that any alcohol radical can be replaced by any other in these substituted quinones, if the substance is

treated with the proper sodic alcoholate,[1] and therefore that the isolation of mixed hemiacetals containing one radical on the ring and another in the acetal part of the molecule would be a matter of great difficulty. These experiments were in fact undertaken to explain the failure of our work on such mixed hemiacetals and acetals, which we had tried to prepare, because we hoped that the conversion of them into the corresponding oxides would throw some light on the constitution of these latter bodies. Our attempts to make the dimethoxyquinone-diethyldibenzoylacetal led to the diethoxydiethyl body as the principal product, but probably a small quantity of the mixed acetal was also formed, as the crude product began to melt at 130°, and it was only after many crystallizations that the pure diethoxydiethylacetal melting at 170° could be obtained.

Action of Isoamylamine on the Oxide,
$C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3$.

Three grams of the oxide were dissolved in hot benzol, and 4.5 grams of free isoamylamine were added with constant stirring. A reaction took place at once with the formation of a yellow precipitate so abundant that the contents of the beaker became almost solid. As this yellow substance is very unstable, we devoted our attention at first to the product of its decomposition, which was more easily obtained and purified. To bring about the decomposition the mixture was heated gently, when the yellow color changed to a purplish red, and the greater part of the solid went into solution, but was deposited as the benzol cooled. The purplish-red solid thus obtained was washed with benzol, and then with water, after which it was purified by recrystallization from hot benzol, to which a very little methyl alcohol had been added. It was then dried at 100° and analyzed with the following results:

I. 0.1089 gram of the substance gave, by combustion, 0.2085 gram of carbonic dioxide and 0.0715 gram of water.

II. 0.1147 gram of the substance gave, by the method of Carius, 0.0931 gram of argentic chloride.

[1] Replacements similar to these have been observed with other classes of bodies by Friedel and Crafts, Ann. Chem. (Liebig). **133,** 208; Israel, *Ibid*, **231,** 220; Isbert, *Ibid*, **234,** 160; Peters, *Ibid*, **257,** 353; Purdie, Ber. d. chem. Ges., **20,** 1554; Bertoni, Gaz. Chim., **12,** 435; **15,** 361; and Gattermann and Ritschke, Ber. d. chem. Ges., **23,** 1738 (1890).

III. 0.1216 gram of the substance gave 0.0969 gram of argentic chloride.

	Calculated for $C_6Cl_2C_5H_{11}NHONH_2C_5H_{11}O_2$.	Found. I.	II.	III.
Carbon	52.60	52.22	....	....
Hydrogen	7.19	7.29	....	....
Chlorine	19.45	....	20.06	19.71

These results show that the substance is the isoamylamine salt of the dichlorisoamylamidoxyquinone. The formation of such a body from the oxide can be explained by the following reactions :[1] In the first place, the addition of 1 molecule of isoamylamine to the atom of oxygen forming

$$C_6Cl_2OCH_2OH(C_5H_{11}NH)(OCOC_6H_5)_2OCH_3;$$

next, the replacement of the methoxy group by an isoamylamido group, and the addition of a molecule of isoamylamine to the hydroxyl giving a complex substance, which must have had this formula :

$$C_6Cl_2(C_5H_{11}NH)(OHNH_2C_5H_{11})C_5H_{11}NH(OCOC_6H_5)_2OCH_3.$$

This would finally be decomposed by the removal of benzisoamylamide and methyl benzoate leaving the body analyzed,

$$C_6Cl_2C_5H_{11}NHOHC_5H_{11}NH_2O_2.$$

That the methoxy group can be replaced by the isoamylamido radical and the substituted acetal saponified to the quinone under these conditions will be proved by some experiments described later in this paper.

Properties of the Isoamylamine Salt of Dichlorisoamylamidoxyquinone, $C_6Cl_2(C_5H_{11}NH)(OHNH_2C_5H_{11})O_2$.—This substance, when crystallized from a mixture of benzol and methyl alcohol, appears in purplish-red needles, which, when examined with the microscope, are seen to be long, very slender, spindle-shaped plates or flattened needles of a pale-purple color. When heated it decomposes into the free phenol melting at its usual temperature, 188°, and isoamylamine, which could be seen coating the upper parts of the melting-

[1] These reactions are arranged in the order which we think will be most easily understood. We do not mean to imply that they took place in this order ; in fact, our work on the yellow product seems to indicate that they did not.

tube, and was recognized by its odor. It is easily soluble in methyl or ethyl alcohol; soluble in acetone, or acetate of ethyl; slightly soluble in cold benzol, or chloroform, more soluble in either of these solvents when hot; insoluble in ether, ligroïn, carbonic disulphide, or water; glacial acetic acid dissolves it, but nothing is precipitated from this solution by the addition of water. All of its solutions show a purple color. The best solvent for it is a mixture of benzol and a little methyl alcohol. Dilute hydrochloric acid, or nitric acid, converts it into a black powder. If a strong acid is used, a red solution is formed, from which water precipitates the black substance. The most convenient way of obtaining the black body is by adding dilute hydrochloric acid to an alcoholic solution of the salt, when it is precipitated. It is the free phenol, $C_6Cl_2(C_5H_{11}NH)OHO_2$, which is described later in this paper. An aqueous solution of sodic hydrate does not dissolve the substance, but, if the alkali is added to an alcoholic solution of the salt, a light-colored compound is precipitated, and at the same time the odor of an amine is observed; heavy white fumes are produced, when hydrochloric acid vapors are brought near the vessel containing this mixture. The precipitate is therefore probably the sodium salt, but it was not thought worth while to study it. Baric chloride gives a violet precipitate, argentic nitrate a red gelatinous precipitate, when added to an alcoholic solution of the salt. These precipitates were more carefully studied in order to characterize the substance more thoroughly.

Silver Salt of Dichlorisoamylamidoxyquinone,
$C_6Cl_2(C_5H_{11}NH)OAgO_2.2H_2O$.

This salt was prepared by adding to a dilute alcoholic solution of the isoamylamine salt an aqueous solution of argentic nitrate in excess. After stirring the solution for some time a mass of olive-gray needles separated, which were collected on a filter, washed very thoroughly with water, and with a mixture of alcohol and water, sucked dry on the filter-pump, and then dried in a desiccator over sulphuric acid to a constant weight. The analysis of the salt gave the following results:

0.1387 gram of the salt, dried in a desiccator, lost 0.0124 gram of water when heated to 105°–110°.

	Calculated for $C_6Cl_2(C_6H_{11}NH)OAgO_2.2H_2O$.	Found.
Water	8.58	8.94

The amount of silver in the salt dried at 105°–110° was determined by heating it in a sealed tube with nitric acid (specific gravity 1.5) and weighing the argentic chloride formed.

I. 0.1223 gram of the substance gave 0.0459 gram of argentic chloride.

II. 0.1866 gram of the substance gave, by the method of Carius (with an excess of argentic nitrate), 0.1425 gram of argentic chloride.

	Calculated for $C_6Cl_2(C_6H_{11}NH)OAgO_2$.	Found. I.	Found. II.
Silver	28.05	28.18	....
Chlorine	18.44	....	18.88

Properties of the Silver Salt.—If in making this salt the argentic nitrate is added slowly to a cold dilute solution of the isoamylamine salt, and the separation takes place slowly, the salt is obtained in olive-gray needles, which contain 2 molecules of water of crystallization, as shown by the analysis given above. These needles, when heated to 110°, lose the water of crystallization, and turn red. If, on the other hand, the solution of argentic nitrate is added to a warm concentrated solution of the isoamylamine salt, a red gelatinous precipitate is obtained, which looks very much like currant jelly, and to judge from its color consists of the anhydrous salt. The red gelatinous mass showed a tendency to pass over into the gray crystalline form; and the red amorphous body could be obtained from the gray needles by dissolving them in a hot mixture of alcohol and water, and cooling rapidly. The crystallized salt is very slightly soluble in cold water, more so in hot; slightly soluble in alcohol. The red amorphous form is insoluble in either water or alcohol.

The colorless filtrate from the olive-gray crystals obtained in the preparation of the silver salt was treated with sodic hydrate, when a strong smell of isoamylamine was observed,

showing that the atom of silver had replaced the molecule of isoamylamine in the original salt, as was to be expected.

Barium Salt of Dichlorisoamylamidoxyquinone,
$[C_6Cl_2(C_5H_{11}NH)OO_2]_2Ba.2H_2O$.

This salt was prepared by adding a dilute solution of baric chloride to the isoamylamine salt, dissolved in cold alcohol. The purplish precipitate was collected on a filter, and washed first with alcohol, and afterward with water, until the wash-water gave no test for a chloride. It was then dried *in vacuo* over calcic chloride, and analyzed with the following results:

0.2063 gram of the salt dried *in vacuo* lost 0.0100 gram of water when heated to 110°.

	Calculated for $[C_6Cl_2(C_5H_{11}NH)OO_2]_2Ba.2H_2O$.	Found.
Water	4.95	4.85

0.1958 gram of the salt dried at 110° gave 0.0641 gram of baric sulphate.

	Calculated for $[C_6Cl_2(C_5H_{11}NH)OO_2]_2Ba$.	Found.
Barium	19.83	19.25

Properties of the Barium Salt.—It consists of crystalline plates of a violet color, which are slightly soluble in cold water, more soluble in hot, but insoluble in alcohol. A dilute solution of the salt gives the black, free oxyquinone on addition of hydrochloric acid.

Dichlorisoamylamidoxyquinone, $C_6Cl_2(C_5H_{11}NH)OHO_2$.

This substance is formed whenever one of its salts is treated with dilute hydrochloric acid. It was prepared for analysis by adding dilute hydrochloric acid to a solution of the purple isoamylamine salt in warm alcohol; the black precipitate thus obtained was washed thoroughly with water, and then crystallized from hot benzol, until it showed the constant melting-point 188°, when it was dried at 100°, and analyzed with the following results:

0.1756 gram of the substance gave, by the method of Carius, 0.1832 gram of argentic chloride.

	Calculated for $C_6Cl_2(C_6H_{11}NH)OHO_2$.	Found.
Chlorine	25.54	25.80

Properties of Dichlorisoamylamidoxyquinone.—The substance forms bronze-black, flattened needles, or long plates. When crystallized from hot alcohol and examined with the microscope, rhombic plates are sometimes observed, which are more usually united into short and broad plates looking like an hour glass; these crystals have a brownish-yellow color, but look black when in thick layers, as, for instance, when two plates overlap, the portions in contact with each other look black, while the other parts of both plates are brownish-yellow, thus giving a very characteristic effect. As the crystallization continues, the hour-glass forms develop into the long plates mentioned at first. It melts at 188°; it is soluble in methyl or ethyl alcohol, benzol, chloroform, ether, or acetone; slightly soluble in ligroïn; very slightly soluble in carbonic disulphide. Benzol is the best solvent for it. Its solutions show a purple color. Strong sulphuric acid dissolves it with a purple color, but the original substance is precipitated from this solution by dilution with water. Sodic hydrate dissolves it, forming a purple solution, from which acids throw down the unaltered substance. The properties of the substance, therefore, confirm the inference drawn from its preparation and analysis, that this is the free oxyquinone.

Yellow Product of the Action of Isoamylamine on the Oxide.

In the description of the action of isoamylamine on the oxide it was stated that a yellow substance was formed at first, which was converted by heating the mixture into the purple isoamylamine salt of the dichlorisoamylamidoxyquinone. It would have been interesting to determine the composition of this intermediate product between the salt and the oxide, but unfortunately it was so unstable, and its properties rendered its purification so doubtful, that we can make no certain statement in regard to it.

It was prepared by dissolving 0.5 gram of the oxide,

$$C_6Cl_2OCH_2O(OCOC_6H_5)_2OCH_2,$$

in a large quantity of benzol, and adding with continual stir-

ring 0.6 gram of isoamylamine. The solution immediately turned yellow, and after standing for a minute or two suddenly began to coagulate, and finally solidified entirely into a yellow, gelatinous mass with a slight, greenish fluorescence. It was washed on a filter with benzol, until the filtrate, which was red at first, became colorless, and was then dried on a porous plate, but as it darkened somewhat, it was washed again with chloroform and alcohol, until it was yellow throughout. After drying *in vacuo* an analysis was made, which gave 16.66 per cent. of chlorine. This is not far removed from 15.93, the percentage of chlorine in the not improbable intermediate compound,

$$C_6Cl_2CH_2O(OHNH_2C_5H_{11})O(OCOC_6H_5)OCH_3,$$

in which one of the acetal groups has been saponified to a quinone oxygen. We did not attempt to get more analyses of this substance, because, owing to its instability and amorphous character, we did not feel that much confidence could be placed in them, and therefore preferred to devote our time to work which had a more immediate bearing on the nature of the oxide, and also promised to give more trustworthy results.

Action of Isoamylamine on Chloranil. Dichlordiisoamylamidoquinone, $C_6Cl_2(C_5H_{11}NH)_2O_2$.

The work described in this and the two following sections of the paper was undertaken to obtain bodies closely related to our isoamylamine salt of dichlorisoamylamidoxyquinone, the study of which might throw some light on the formation of that body.

Two grams of chloranil were dissolved in hot benzol, and heated with two grams of isoamylamine with constant stirring. At first a green coloration was noticed, similar to that obtained by the action of sodic alcoholates on chloranil, but on longer heating of the mixture this green color gave place to a purple, and, on cooling, beautiful purple plates separated from the solution. The substance was washed thoroughly with alcohol to remove a white impurity, probably the chloride of isoamylamine, which had separated with it, and then

recrystallized from benzol until it showed the constant melting-point 224°–225°, when it was dried at 100°, and analyzed with the following result:

0.1786 gram of the substance gave, by the method of Carius, 0.1500 gram of argentic chloride.

	Calculated for $C_6Cl_2(C_6H_{11}NH)_2O_2$.	Found.
Chlorine	20.46	20.76

Properties of Dichlordiisoamylamidoquinone.—The substance crystallizes in long plates or flattened needles terminated by a single plane at a not very oblique angle to the sides. The color is a dark red, and the crystals often show a marked purple iridescence when separating from solution. It melts at 224°–225°. It is slightly soluble in cold benzol, more freely in hot; almost insoluble in alcohol; insoluble in water. The best solvent for it is benzol. Strong hydrochloric acid has no apparent action on it; strong sulphuric acid dissolves it, but the original red body is precipitated on the addition of water.

Action of Isoamylamine on Dichlordimethoxyquinonedimethyldibenzoylacetal.

To study this action 0.7 gram of the acetal was dissolved in hot benzol, mixed with 1.1 grams of isoamylamine, and the mixture heated to boiling on the steam-bath. On cooling, crystals were deposited similar in appearance to those obtained by acting on chloranil with isoamylamine. After crystallization from benzol they melted at 224°–225°, and therefore were the dichlordiisoamylamidoquinone, with which the substance also agreed in its other properties. Dichlordimethoxyquinone also gives this same product, when treated with isoamylamine.

These experiments show that the methoxy radical in these substituted quinones can be replaced by the isoamylamido group, when the quinone is heated with isoamylamine, and also that isoamylamine can convert a benzoylmethylacetal into the corresponding quinone, two points which are of great importance in interpreting the transformations of the oxide, $C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3$, under the influence of isoamylamine.

Isoamylamine Salt of Chloranilic Acid,
$C_6Cl_2(OHNH_2C_5H_{11})_2O_2$.

This salt was made by dissolving a small quantity of chloranilic acid in warm alcohol, and adding a slight excess of isoamylamine; the salt appeared as an abundant, purplish-red precipitate, which was purified by washing it with benzol, alcohol, and water. It was dried at 110°, and gave the following results on analysis:

I. 0.1307 gram of the salt gave, by the method of Carius, 0.0992 gram of argentic chloride.

II. 0.2208 gram of the salt gave 0.1672 gram of argentic chloride.

	Calculated for $C_6Cl_2(OHNH_2C_5H_{11})_2O_2$.	Found. I.	II.
Chlorine	18.54	18.77	18.72

Properties of the Isoamylamine Chloranilate.—It is a purplish-red, crystalline substance; slightly soluble in methyl or ethyl alcohol; also somewhat soluble in glacial acetic acid, but decomposed by it; essentially insoluble in benzol, ether, chloroform, acetone, ligroïn, carbonic disulphide, or ethyl acetate. Hydrochloric acid decomposes the salt, giving a solution of chloranilic acid, which was recognized by the purple color of its aqueous solution, and the formation from this solution of the characteristic red silver salt.

Action of Diisoamylamine on the Oxide,
$C_6Cl_2OCH_2O(OCOC_5H_9)_2OCH_2$.

After the study of the action of isoamylamine on the oxide, which has been just described, it seemed of interest to determine whether a secondary amine would act like a primary amine on the oxide, and accordingly we took up this work with diisoamylamine.

When to 1 gram of the oxide dissolved in hot benzol 2.5 grams of diisoamylamine were added, the solution turned yellow immediately, and this color finally gave place to red. On cooling, no solid separated, but after evaporating off part of the solvent a reddish compound appeared. To obtain this in quantity the greater part of the benzol was evaporated off on the steam-bath, and the rest was allowed to pass off spon-

taneously. The red solid left was washed thoroughly with water, and purified by crystallization, at first from a mixture of alcohol and water, and finally from ligroïn, until it showed the constant melting-point 168°–169°, when it was dried at 100°, and analyzed with the following result :

0.1245 gram of the substance gave, by the method of Carius, 0.0714 gram of argentic chloride.

	Calculated for $C_6Cl_2(C_5H_{11})_2N(OHNH(C_5H_{11})_2)O_2$.	Found.
Chlorine	14.06	14.17

Properties of the Diisoamylamine Salt of the Dichlordidiisoamylamidoxyquinone.—It separates from hot ligroïn in reddish-brown crystals, which melt at 168°–169°. It is very soluble in acetone, benzol, or chloroform ; soluble in cold alcohol, easily soluble in hot ; somewhat soluble in cold ligroïn, more freely in hot. The addition of an acid to the alcoholic solution sets free the oxyquinone, which usually is precipitated as an oil. Plumbic acetate, when added to the alcoholic solution, gave a greenish precipitate.

As the analysis and properties of this substance showed that diisoamylamine had acted on the oxide in precisely the same way as the isoamylamine, we decided not to pursue this line of work further.

Action of Diisoamylamine on Chloranil.

A small quantity of chloranil dissolved in hot benzol was treated with an excess of diisoamylamine. A green coloration was first noticed, which changed to brown in a short time, while a white crystalline substance was precipitated, which was recognized as the chloride of diisoamylamine by its properties. After the solution had been evaporated to a slight extent on the steam-bath, the insoluble diisoamylamine salt was filtered out, and the filtrate mixed with its own volume of alcohol allowed to evaporate spontaneously. After several hours, beautiful, purplish-black needles separated from the liquid, which were washed with alcohol, and finally recrystallized from alcohol. After drying *in vacuo* it gave the following result on analysis :

0.0971 gram of the substance gave, by the method of Carius, 0.0577 gram of argentic chloride.

	Calculated for $C_6Cl_2[(C_5H_{11})_2N]_2O_2$.	Found.
Chlorine	14.58	14.69

It is evident, therefore, that the diisoamylamine has acted on chloranil in the same way that isoamylamine acted.

Properties of Dichlordidiisoamylamidoquinone, $C_6Cl_2[(C_5H_{11})_2N]_2O_2$.—It crystallizes from alcohol in long, reddish-black needles. The substance is far from stable, giving off an odor of diisoamylamine on standing in the air or in a desiccator. If exposed to the air for a long time, it turns first reddish-brown, and finally becomes an uninviting sticky mass. Owing to this slight stability we are unable to state its melting-point with certainty; the highest melting-point observed for it was 77°–78°. It is very easily soluble in benzol, ether, ligroïn, carbonic disulphide, or chloroform; soluble in alcohol or acetone; insoluble in water. Alcohol is the best solvent for it. It dissolves in strong sulphuric acid, and this solution gives a precipitate, when diluted with water. Cold sodic hydrate has no apparent action on it.

Action of Phenylhydrazine on the Oxide, $C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3$.

When the oxide is warmed gently with phenylhydrazine a yellow substance is formed, which recalls the yellow intermediate body formed by the action of isoamylamine on the oxide. Before we found that isoamylamine led to definite compounds with comparative ease, we devoted a great deal of time to the study of this phenylhydrazine product and its derivatives, but with no result of sufficient certainty to be described, for, although more stable than the yellow isoamylamine compound, this phenylhydrazine derivative is not stable enough to give good results on analysis. So far as our work has led to any formulas they are in harmony with what we should expect from our study of the behavior of isoamylamine.

Hydroxylamine apparently does not act on the oxide.

Dichlordimethoxyquinonedimethyldiacetylacetal,
$C_6Cl_2(OCH_3)_2(OCOCH_3)_2(OCH_3)_2$.

This substance and the ethyl compound described in the next section were prepared for the sake of comparison with the corresponding benzoyl acetals.

3.5 grams of the sodium salt of the dichlordimethoxyquinonedimethylhemiacetal were suspended in acetone, and 2 grams of acetyl chloride added with constant stirring. The action took place to some extent even in the cold, but to complete it the mixture was heated on the steam-bath for a short time, until most of the acetone had passed off. The product thus obtained was crystalline, and somewhat colored by chloranilic acid and dichlordimethoxyquinone. It was purified by washing with alcohol, water, and dilute sodic hydrate, to remove sodic chloride, chloranilic acid, and the red substituted quinone, and at last by crystallization from a mixture of chloroform and alcohol, until it showed the constant melting-point 177°–178°, when it was dried at 100°, and analyzed with the following result:

0.2031 gram of the substance gave, by the method of Carius, 0.1534 gram of argentic chloride.

	Calculated for $C_6Cl_2(OCH_3)_2(OCOCH_3)_2(OCH_3)_2$.	Found.
Chlorine	18.44	18.67

Properties of Dichlordimethoxyquinonedimethyldiacetylacetal.— The substance crystallizes from a mixture of chloroform and alcohol in good-sized, white prisms, in which two basal planes are usually so well developed that the crystals look like thick plates. The edges also consist of two basal planes commonly, and the ends of two planes at an obtuse angle to each other. The form seems to be monoclinic. Another very common form consists of rhombic plates with bevelled edges and very sharp acute angles, which are frequently truncated by 2 planes, the enlargement of these planes forming the edges in the prisms described at first. It melts at 177°–178°.[1] It is easily soluble in chloroform; soluble in benzol; slightly soluble in ethyl or methyl alcohol, but more soluble in either of these solvents when hot; slightly soluble in ether

[1] The corresponding benzoyl compound melts at 193°.

or acetone; almost insoluble in glacial acetic acid; essentially insoluble in ligroïn, carbonic disulphide, or water. A mixture of chloroform and alcohol is the best solvent for it. Sodic hydrate has no apparent action on it.

The most interesting work with this substance was to try to convert it into an oxide similar to the one obtained from the benzoyl acetal. For this purpose it was heated with sulphuric acid of specific gravity 1.44, but the only product which seemed to be formed in these experiments was chloranilic acid; no signs of an intermediate substance could be found. It appears, therefore, that the acetyl groups are far less firmly attached to the molecule in this class of compounds than the benzoyl groups.

Dichlordiethoxyquinonediethyldiacetylacetal,
$C_6Cl_2(OC_2H_5)_2(OCOCH_3)_2(OC_2H_5)_2$.

Six grams of the sodium salt of dichlordiethoxyquinonediethylhemiacetal were suspended in a little acetone, and treated with 3 grams of acetyl chloride with constant stirring. The reaction took place even in the cold, but in order to be certain that it was complete the mixture was heated gently on the steam-bath for a few minutes. The product was washed with water, dilute sodic hydrate, and finally with a little alcohol, after which it was crystallized from a mixture of chloroform and alcohol, until it showed the constant melting-point 120°–121°, when it was dried, and analyzed with the following results:

I. 0.2059 gram of the substance gave, by the method of Carius, 0.1356 gram of argentic chloride.

II. 0.1740 gram of the substance gave 0.1126 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_2H_5)_2(OCOCH_3)_2(OC_2H_5)_2$.	Found. I.	II.
Chlorine	16.09	16.28	16.00

Properties of Dichlordiethoxyquinonediacetyldiethylacetal.— This substance crystallizes from a mixture of chloroform and alcohol in very sharp rhombic plates with bevelled edges, and the acute angles often truncated. It resembles the methyl compound strongly in crystalline form and habit except that

the plates are usually thinner, and it crystallizes even more beautifully. It melts at 120°–121°,[1] and is soluble in benzol or chloroform; somewhat soluble in carbonic disulphide; slightly soluble in cold methyl or ethyl alcohol, more soluble in hot; insoluble in ligroïn or in water. A mixture of chloroform and alcohol is the best solvent for it. Sodic hydrate has no apparent action upon it.

Action of Sulphuric Acid on Certain Diatomic Phenols.

This work was undertaken in the hope that it might give some help in deciding whether the atom of oxygen in the oxide of dichlormethoxyquinonedibenzoylmethylacetal is in the ortho or meta position; for if by treating ortho or meta diatomic phenols with sulphuric acid we could obtain from the one or the other an oxide similar to that which we are studying, there would be a strong probability that the oxygen in our oxide was attached in the same position as that in the new oxide.

The phenols which we have used are resorcine as the meta body, pyrocatechine and some of its derivatives as the ortho compounds, and also chloranilic acid as a representative of the para series.

The sulphuric acid of specific gravity 1.44 used in making the oxide, $C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3$, had no apparent effect on resorcine, but when it was boiled with an acid of specific gravity 1.71, a reddish-brown solution was formed, which deposited a brown mass on cooling; this dissolved in sodic hydrate, and was reprecipitated by hydrochloric acid. From its properties there can be little doubt that it is the resorcine ether, $(C_6H_4OH)_2O$, and therefore that 2 molecules of resorcine have taken part in its formation.

Sulphuric acid of specific gravity 1.44 had no apparent effect on chloranilic acid.

Sulphuric acid of 1.44 specific gravity did not act on pyrocatechine, and when an acid of 1.84 specific gravity was used the substance was charred. When guaiacol was boiled with sulphuric acid of specific gravity 1.44 for three to four hours, the liquid turned purplish-black, and on standing a small quantity of a

[1] The corresponding benzoyl compound melts at 170°.

black amorphous substance separated, which we have not yet succeeded in obtaining in sufficient quantity for identification; but, as it became colorless when treated with zinc and sulphuric acid, and this reduction-product was turned yellow by dilute nitric acid, it seems certain that it is not the desired oxide. It probably belongs to the class of quinones. We hope that the study of this body will be continued in this laboratory in the coming year. In the hope that the loading of the benzol ring with bromine atoms would make the substance more stable, and at the same time encourage the formation of an oxide, since our oxide was prepared from a body with negative radicals on the ring, we next tried the action of sulphuric acid on tetrabromveratrol. With weaker acids no change was observed, but, when it was heated with an acid of specific gravity 1.84, a dark-colored solution was formed, and sulphurous dioxide was given off; after dilution with water a red substance was precipitated, which we inferred was tetrabromorthoquinone from its color, and the fact that the sulphuric acid had given up oxygen in forming it. We have not succeeded as yet in obtaining anything resembling our oxide from any of the other brompyrocatechines or their ethers which we have tried.

Tetrabromguaiacol, $C_6Br_4OCH_3OH$.

This substance was made in connection with the work just described, as follows: Five cc. of bromine (a considerable excess over the 4 molecules required) were added slowly to 2 grams of guaiacol. The reaction was very violent, hydrobromic acid being given off copiously, and before all the bromine had been added the oil solidified to a white mass. After the reaction had been rendered complete by heating for a short time on the steam-bath, the product was crystallized from hot chloroform, until it showed the constant melting-point 162°–163°. The same substance was obtained by adding the guaiacol to the bromine. It was dried at 100°, and analyzed with the following result:

0.2635 gram of the substance gave, by the method of Carius, 0.4485 gram of argentic bromide.

	Calculated for $C_6Br_4OCH_3OH$.	Found.
Bromine	72.71	72.44

Properties of Tetrabromguaiacol.—It crystallizes from chloroform in long, white, slender prisms, or thick needles with square ends; and melts at 162°–163°. It is easily soluble in acetone or ether; soluble in ethyl or methyl alcohol, or in chloroform, much more soluble in hot than in cold chloroform; somewhat soluble in benzol, or carbonic disulphide; slightly soluble in glacial acetic acid, or ligroïn; insoluble in water. It dissolves easily in an alcoholic solution of sodic hydrate; and in an aqueous solution of sodic hydrate, if it is hot. Acids precipitate the unaltered substance from either of these solutions. When a solution of tetrabromguaiacol in warm glacial acetic acid is treated with strong nitric acid, a red body is formed which we think is tetrabromorthoquinone.

Tribromveratrol, $C_6HBr_3(OCH_3)_2$.

This substance was prepared from tribromguaiacol made by the action of bromine on an alcoholic solution of guaiacol according to Tiemann and Koppe.[1] 4 grams of the tribromguaiacol were heated in a flask with a return-condenser with 0.45 gram of sodic hydrate dissolved in about 50 cc. of methyl alcohol and an excess of methyl iodide. After heating for about an hour the solution was concentrated somewhat on the steam-bath, when upon cooling a large quantity of white crystals separated. These were washed with dilute sodic hydrate to remove any unaltered tribromguaiacol, and then with water; after which they were recrystallized from alcohol until they showed the constant melting-point 86°–87°, when the substance was dried *in vacuo*, and analyzed with the following results:

I. 0.2094 gram of the substance gave, by the method of Carius, 0.3108 gram of argentic bromide.

II. 0.1196 gram of the substance gave 0.1795 gram of argentic bromide.

[1] Ber. d. chem. Ges., 14, 2017.

	Calculated for $C_6HBr_3(OCH_3)_2$.	Found. I.	II.
Bromine	64.00	63.19	63.87

Properties of Tribromveratrol.—It crystallizes from hot alcohol in long, slender, slightly branched, white needles, which when well developed have blunt, perhaps square, ends. It melts at 86°–87°. It is easily soluble in benzol, chloroform, acetone, or ethyl acetate; soluble in ligroïn; somewhat soluble in methyl or ethyl alcohol, or in glacial acetic acid, much more soluble in each of these solvents when hot. The best solvent for it is hot alcohol. Sodic hydrate does not dissolve it, and does not decompose it even when boiling. A warm, glacial acetic acid solution of tribromveratrol turns bright-red, when strong nitric acid is added to it. If tribromguaiacol is treated in the same way, a similar red color is produced, and a bright-red substance is deposited on cooling, which we supposed was tribromorthoquinone, but owing to the small yield and the late date at which this work was undertaken we are unable to make any definite statement in regard to it. We hope that the study of this substance will be continued in this laboratory during the coming year.

Colored Compounds Obtained from Substituted Quinones by the Action of Sodic Alcoholates.

The work described in this section was undertaken in the hope of preparing new hemiacetals derived from the substituted quinones, and also of throwing more light on the nature of quinhydrone and phenoquinone. It was abandoned before it had reached a satisfactory conclusion, because of the appearance of two papers by Astre,[1] in which he described substances similar to those made by us; but we give an account of it here, as it has led us to differ from Astre in regard to the constitution of these bodies.

In the paper[2] on hemiacetals derived from quinones, Grindley and one of us state that the first product of the action of sodic phenylate on chloranil is a green or black substance, which on heating passes rapidly into the red dichlordiphenoxyquinone. As it seemed possible that this might be a diphenyl-

[1] Compt. rend., **121**, 326, 530. [2] This JOURNAL, **17**, 595.

hemiacetal, we spent some time in trying to isolate it; but, although we succeeded in obtaining a dark-green substance in the solid state, we were unable to find any method of freeing it from the sodic chloride, which (in addition to dichlordiphenoxyquinone) was always formed by a secondary reaction, since it was very unstable. We next turned our attention to the green compound formed by the action of sodic methylate on chloranil,[1] as this from its mode of formation and color seemed to be analogous to the phenoxy compound. Here we were more successful. A sample of this green product of the action of sodic methylate on chloranil was washed with equal parts of methyl alcohol and water, which did not decompose it so rapidly as water alone, then with methyl alcohol alone, and finally with benzol. It gave the following result on analysis, after it had been dried *in vacuo*:

0.1810 gram of the substance gave 0.0418 gram of sodic sulphate.

	Calculated for $C_4Cl_4O_2CH_3ONa$.	Found.
Sodium	7.66	7.48

Our other analyses pointed to a similar composition for this substance and related compounds, but in no other case were we so fortunate as to obtain a sample free from sodic chloride. We should not venture to publish this single analysis, therefore, if it were not confirmed by the results given by Astre, who made a green compound by the action of potassic ethylate in ethereal solution upon quinone, which had the formula $C_6H_4O_2KOC_2H_5$, and a similar substance with alcoholic potassic hydrate, $C_6H_4O_2KOH$. Our attempts to prepare compounds like these for analysis have given us a high appreciation of the experimental skill which Astre has shown in purifying these substances. That his compounds are analogous to ours we think can admit of no doubt; not only on account of the analyses, but from the method of formation and the color.

Astre, however, does not assign to his compounds the formulas given above, but considers that the potassium has replaced one of the atoms of hydrogen attached to the benzol

[1] This JOURNAL, 17, 602.

ring, so that the substances contain alcohol or water of crystallization, thus: $C_6H_3KO_3C_2H_5OH$ and $C_6H_4KO_3H_2O$. His principal reason for this is based on his experiment with metallic potassium and an ethereal solution of quinone. In this case he found that hydrogen was given off, and a green compound formed having the formula $(C_6H_4KOOH)_2C_4H_{10}O$, which amounts to a molecule of dipotassic quinhydrone combined with one molecule of ether. The attempt to apply Astre's theory to our compound leads to the inadmissible formula $C_6Cl_4NaO_2CH_2OCl$, and therefore, if his compounds and ours are similarly constituted, his theory must be abandoned. In this case it is necessary to explain his result with metallic potassium and quinone in ethereal solution, and this can be done perhaps by supposing a very minute quantity of water or alcohol to have been present in the ether used. This would have given nascent hydrogen, which would have formed a little quinhydrone; this quinhydrone then, by acting on the potassium, would give its salt and more nascent hydrogen, which would continue the action, until a considerable amount of the potassium salt of the quinhydrone had been formed. As quinhydrone forms salts with the metal probably attached to oxygen,[1] it is not necessary to assume that the atom of potassium has replaced the hydrogen on the benzol ring in this case. All these compounds, by their mode of formation, marked colors, and slight stability, recall the substances formed by the action of sodic alcoholates on various nitro compounds, (such as trinitrobenzol,[2] symmetrical dinitrobenzoic acid,[3] bromdinitrobenzoic acid, and bromdinitrotoluol,[4]) and we think probably belong to the same class. The lamented Victor Meyer had already proposed a theory to account for these substances similar to that of Astre, since he assumed that an atom of hydrogen on the benzol ring was replaced by sodium in these bodies, but it is hard to bring this theory into accord with some of the facts published since it was proposed, and the whole subject needs further investigation.

[1] Jackson and Oenslager: This JOURNAL, **18**, 15.
[2] Lobry de Bruyn: Rec. Trav. Chim. Pays-Bas., **14**, 89.
[3] Victor Meyer: Ber. d. chem. Ges., **27**, 3153.
[4] Jackson and Ittner: This JOURNAL, **19**, 199.

We shall not describe our numerous experiments in regard to these colored derivatives of the quinones, but content ourselves with simply mentioning the substances observed by us. Chloranil gave in addition to the green compounds with sodic methylate and phenylate already mentioned a similar product with sodic amylate. Trichlorquinone also gave a green product with sodic methylate or amylate. Trichlorquinone, or chloranil, gave a blue compound with a strong solution of sodic hydrate, and we also observed the formation of a blue product from sodic hydrate and quinone before the appearance of Astre's paper. With sodic methylate, or amylate, quinone gave blue substances, undoubtedly similar to the ethylate product analyzed by Astre. Hydroquinone gave a faint bluish-green coloration with sodic hydrate in aqueous solution, and a bluish-green color when sodic methylate was added to its solution in benzol.

Action of Iodine and Sodic Hydrate on Chloranilic Acid.

We had hoped to extend our work to the reduction-product obtained from the ethyl oxide by Grindley and one of us,[1] and accordingly tried to reduce the oxide,

$$C_6Cl_2OCH_3O(OCOC_6H_5)OCH_3,$$

with hydriodic acid in the way used for the ethyl oxide, but we found that, whereas the ethyl compound was easily reduced, as described in the place cited, the methyl oxide was not at all affected under the same conditions, and no satisfactory result was obtained, even when much higher temperatures were used. To the product of one of these experiments, which contained unaltered oxide and free iodine, sodic hydrate was added, when a yellow body separated, which had the smell of iodoform. This observation led us to try the action of iodine on an alkaline solution of sodic chloranilate, when we found that even at as low temperatures as 50°–60° iodoform was obtained. This was recognized by its melting-point, 119°, its odor, its yellow color, and the fact that it crystallized in the hexagonal system, although it appeared in stars like snowflakes instead of the usual hexagonal plates.

[1] This JOURNAL, 17, 641.

The work with the reduction-product was begun so late in the year that no definite results were obtained before the close of the laboratory for the vacation.

REVIEWS.

NOZIONI DI ANALISI CHIMICA E CENNI SULL' ANALISI DELLE ACQUE POTABILI, del DOTT. ICILIO GUARESCHI, professore ordinario di Chimica Farmaceutica e Tossicologica nella R. Università di Torino. Unione Tipografico-editrice. Torino. 1898.

This little book, of 172 pages, is intended to provide an elementary manual of qualitative chemical analysis in general, mainly of inorganic substances, with special chapters on "microchemical" work and on the examination of potable waters. Hence the greater part is necessarily a reproduction, with but little novelty of form, of what has appeared in numberless other manuals in various languages.

A few points give a certain degree of originality to the mode of treatment of the well-worn subject. Thus, in the preliminary chapter devoted to "nozioni generali," the nature of the reactions made use of for analytical purposes is stated with rather more fulness than in many books, including reference to such matters as the modern ideas of dissociation of *ions* in solution, chemical stability and activity under varying physical conditions, etc. Among the directions for the identification of individual basic and acid radicles a few reactions are mentioned which are not in general use, as, for instance, the detection of mercury in mercuric salts by the formation of the blue crystalline double thiocyanate of mercury and cobalt, and a few substances are to be found here which are not very commonly included in the list of those to be detected, such as trichloracetic and lactic acids.

In the chapter on microchemical analysis there are some useful suggestions as to the production of crystalline precipitates easily recognizable by their microscopic appearance, including some rather unusual substances, such as the antimonio-tartrate of barium, and the double acetate of uranyl and sodium. Throughout the work there are numerous and, in general, good figures of specimens as seen under the microscope. The only part in which quantitative methods are discussed is that on the examination of natural waters for domestic use.

Although the name of Professor Guareschi, of the University of Turin, appears on the title-page, the book seems to have been prepared by other hands from notes of his lectures and laboratory teachings. J. W. M.

THERMOCHIMIE, À PROPOS D' UN LIVRE RÉCENT DE M. MARCELLIN BERTHELOT, par P. DUHEM, professeur de physique théorique à la Faculté des Sciences de l'Université de Bordeaux. (Extrait de la Revue des Questions Scientifiques, Octobre, 1897.) Librairie Scientifique A. Hermann. Paris. 1897.

This rather polemical criticism of the work by Berthelot, published last year under the title "Thermochimie—Données et lois numériques," reviewing it in contrast with the work put forth in 1879 by the same author, with the title "Essai de Mécanique chimique, fondée sur la Thermochimie," is worth reading, although the tone is not altogether to be admired.

M. Duhem's view of the life work of Berthelot is summed up in the sentence—"Parvenu au terme de sa carrière, M. Berthelot constate que les buts qu' il s'est laborieusement efforcé d' atteindre étaient des chimères, que les idées auxquelles il s'était passionnément attaché étaient des erreurs, que le temps, que les efforts qu' il a consacrés à défendre ces idées ont été employés à combattre la verité." Any less partial admirer of Sainte-Claire Deville and of Thomsen will hardly do Berthelot the injustice of adopting these words in the full extent of their meaning. And yet it must be admitted that they are not altogether without a kernel of truth. With much of the creative originality of the French pioneer in science, and with prodigious capacity for experimental work, Berthelot has seemed to suffer in unusual degree from inability or unwillingness to look at his own results in any other than one light—especially from refusal to connect them with, or subordinate them to the broader views of matter and energy which, although confessedly imperfect, have so many and such important relations in every direction that no one can afford to completely ignore or neglect them.

His indisposition to entertain as a working hypothesis the "atomic theory" of modern chemists has seemed to close his eyes to at least one cause, perhaps the main cause, of the infertility of his immense assemblage of facts—namely, that his thermal determinations represent only *balances* struck between energy absorbed and evolved, that in no case does he exhibit, nor can anyone as yet exhibit, the thermal effect of an act of simple chemical union or simple chemical separation.

Moreover, in seeking to discriminate between phenomena to be called on the one hand chemical and on the other physical, he no doubt seems to overlook the fact that his results often represent but a single arbitrarily selected set of conditions, and would lose their appearance of generality if these conditions were to be varied.

There are not lacking in M. Duhem's criticism traces of

the oft-encountered one-sidedness which can see, as in the fable of the gold and silver-faced shield, only matter or only energy, though we have ever before us in nature the mysterious association of the two. Yet, as has been said, this critical article is worth reading—not so much for the depreciatory criticism as for the glimpse it gives of the perpetual struggle onwards *towards* truth, with so much toil and so much partially ineffective labor on the part of even the strongest in the army of science. J. W. M.

SPECTRUM ANALYSIS. By JOHN LANDAUER, LL.D. Authorized English edition by J. BISHOP TINGLE. New York: John Wiley & Sons.

As stated in the author's preface, "this work originated as a reprint of an article on Spectrum Analysis recently contributed to Fehling-Hell's 'Neues Handwörterbuch der Chemie.'"

Its object, as explained in the translator's preface, is to fill a gap which has long been felt in the teaching of spectrum analysis as a branch of chemistry. The translator says, "the claim of spectrum analysis to a place in a chemical curriculum is steadily obtaining increased recognition, and its importance is generally admitted both for students preparing for teaching and for those who wish to engage in technological work." He adds that "there has been no attempt to treat the subject exhaustively, but rather to indicate the more salient points of theory, etc., leaving it to the teacher to complete and extend them at his own discretion." The plan of the book may be judged from the contents, which are divided into ten chapters.

Chapter I is introductory and historical.

Chapter II deals with the physical properties of light, such as refraction, dispersion, and diffraction.

Chapter III describes various forms of prismatic and grating spectroscopes.

Chapter IV contains descriptions of spectroscopic instruments and Rowland's concave grating apparatus.

Chapter V contains descriptions of various spectroscopic adjuncts such as are necessary for the investigation of flame-, arc-, spark-, and absorption-spectra.

Chapter VI discusses emission spectra from the physical standpoint, giving an account of Kirchhoff's law and all the laws concerning absorption, fluorescence, etc. In this same chapter also are discussed the various relations which exist between the lines of the spectrum of any one element or between the spectra of different elements.

In chapter VII there are given tables of wave-lengths of all the elements, together with those of many of the compounds.

Chapter VIII deals with absorption-spectra, giving the results of the best investigations.

Chapter IX discusses the solar spectrum, including the results of observations of different portions of the sun and the theories which have resulted from these observations.

Chapter X describes the spectrum of other celestial bodies, such as planets and the fixed stars. There is also a brief account of auroras, of lightning, and the question as to the displacement of lines owing to motion in the line of sight.

It is evident that the scope of the work is very wide, and it may be said in the main that the purposes of the book are well carried out. The translation is excellent and the arrangement of the matter is all that can be desired. The index and the references in the different chapters are most satisfactory. It is a pleasure to have a book so well fitted for actual use as the one before us. The book is in every way well suited for the object for which it is written, namely to serve as a guide for practical laboratory work for students of chemistry; and it is to be recommended most heartily.

There are, however, various points which it is the duty of the reviewer to mention—errors of omission, as well as errors of commission. Some of these could be easily corrected in later editions which it is to be hoped will be called for before many months. The system of abbreviations used throughout the book is most unsatisfactory. The scientific world has become so thoroughly accustomed to the abbreviation "Phil. Mag." for the "Philosophical Magazine," and "Pogg. Ann." for Poggendorf's Annalen," that it is not at all desirable at the present time to change these well-known symbols for such unsuggestive ones as " P. M." and " P. A." An abbreviation ought to have the merit of suggesting something in itself, and such as these, " P. T." and " P. R. S.," etc., are not to be recommended.

Again, in mentioning Scheiner's most excellent treatise on Spectrum Analysis of the Stars, it should be added that there is an English translation by Frost, which in some respects is superior to the German original. There seems to be no reason also, if Higgs's photographic atlas of the normal solar spectrum is mentioned, why Rowland's standard map of the same spectrum should not also be included.

There are various matters of importance which are not mentioned in the book, some of which certainly deserve notice. Among these may be mentioned the use of the radiomicrometer as an instrument of research in the ultra-red spectra; the results of the work by Humphreys and Mohler on the effect of the pressure on the arc, results which are some of

the most important obtained in recent years; the law recently discovered by Rydberg and Schuster on the relations between the different series in the spectrum of any one element; Michelson's work on the constitution of various spectrum lines and his determination of the value of the standard metre in terms of wave-lengths. There are many other matters which one might expect to see discussed, but it may be that the work went to press before the results were well known. These, however, which are mentioned above, certainly ought to appear. It must be said too that from a physical standpoint many of the sections in the book are unsatisfactory. The chapter devoted to prisms and gratings is not at all what might be desired, and in regard to gratings particularly there are several statements which are not correct. It would have been easy to have given an elementary theory of the plane grating, which would have been useful to all students, whatever their acquaintance with physics. The description of the Zeeman effect on page 75 is also incomplete. The section on the absorption of solutions on page 79 is not as full nor as definite as it should be. Within recent years the study of the absorption of solutions has obtained such prominence and measurements are now made so accurately that this subject would seem to demand more careful treatment than it receives here. In several places in the book, too, the spark spectrum is spoken of as having a higher temperature than the arc; a statement which is misleading, because it can hardly be said that a spark has a temperature.

In conclusion, it may be said that the book before us is the most satisfactory of any that is at present available for students. The paper, type, and the illustrations are excellent; and special praise should be again given the references and the index. The book may be placed safely in the hands of all students, and is to be recommended to both teacher and class. J. S. A.

DER PRAXIS DER MOLEKELGEWICHTSBESTIMMUNG. Von HEINRICH BILTZ, Privatdocent an der Universität in Greifswald. Fischer's Medicinische Buchhandlung. H. Kornfeld, Berlin. 1898. pp. 170.

The determination of the molecular weights of substances has become a familar laboratory operation. The methods which apply to the vapors of substances enable us to decide the question, how many molecules are aggregated into a unit when the compound in question is present as a gas, while the freezing-point and boiling-point methods furnish us with the means of ascertaining the molecular weights of substances in solution in a given solvent.

The purpose of the work in hand is to describe and discuss

these methods for the purpose of application in the chemical laboratory. And since complicated cases often arise during the progress of chemical investigations, a comparatively thorough and elaborate treatment of the available methods is deemed necessary by the author.

The determination of the molecular weights of substances in the form of vapor is taken up first, and the methods of Dumas, Gay Lussac, Hofmann, and V. Meyer, are treated of at some length. This is followed by a discussion of the freezing-point and boiling-point methods for determining the molecular weights of substances in solution. The apparatus of Beckmann for carrying out these methods is described, together with various improvements which have been made by different experimenters, for the purpose of increased accuracy.

The book concludes with a description of the method of Traube, for determining the molecular weights of pure substances in the liquid or solid form, from their molecular volumes. But the author states in his preface that "the results must be used with considerable care until the method has been more completely investigated and applied."

One notices the absence of the beautiful method of Ramsay and Shields for determining the molecular weights of liquid substances from their surface-tension. This was probably omitted, because the measurement of surface-tension is not altogether simple, and it can hardly be hoped that this method will ever be generally used in the laboratory.

The book is clear, concise, and in every particular an admirable piece of work. It seems that an English translation would be useful. H. C. J.

DAS OPTISCHE DREHUNGSVERMÖGEN ORGANISCHER SUBSTANZEN UND DESSEN PRAKTISCHE ANWENDUNGEN. Bearbeitet von DR. H. LANDOLT, Professor der Chemie an der Universität zu Berlin. Unter Mitwirkung von DR. O. SCHÖNROCK, DR. P. LINDNER, DR. F. SCHÜTT, DR. L. BERNDT, DR. T. POSNER. Zweite gänzlich umgearbeitete Auflage, mit eingedruckten Abbildungen. Druck und Verlag von Friedrich Vieweg und Sohn. 1898. pp. 655.

The first edition of this book appeared eighteen years ago, when the subject was comparatively undeveloped. The number of active substances known, has not only increased from 300 to more than 700, but optical activity has acquired far deeper significance since van't Hoff and Le Bel pointed out the relation between rotation and constitution.

In this comprehensive work the author distinguishes between three classes of optically active substances. Those which rotate the plane of polarization only when crystalline, those which rotate when either crystalline or amorphous, and

those which are active when amorphous, in the liquid state and in solution. After considering the theory of the asymmetric carbon atom, the methods for obtaining active from inactive substances, involving crystallization, the use of alkaloid salts, and the use of bacteria, are taken up.

The second part of the book deals with the relation between the amount of rotation, and the physical conditions employed, such as wave-length of light, temperature, etc.

The third part of the book is of most direct interest to the physical chemist, since it discusses the problem of the rotation of substances in solution, and thus bears directly upon the theory of electrolytic dissociation.

The fourth part, written by Schönrock, describes exhaustively the forms of apparatus employed in measuring the amount of rotation—the polarizer, saccharimeter, lamps, tubes for holding the liquids, etc.

Schütt has written part 5, on the practical applications of optical rotation—such as the determination of the amount of sugar, glucose, camphor, nicotine, etc.

The sixth, and last, division comprises the data which were obtained up to 1896.

The accuracy and thoroughness of this book are both insured by the name of its author. H. C. J.